8-2006

Free Radical Polymerization in Room Temperature Ionic Liquids

Xiao Ma
University of Tennessee - Knoxville

To the Graduate Council:

I am submitting herewith a thesis written by Xiao Ma entitled "Free Radical Polymerization in Room Temperature Ionic Liquids." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Jimmy W. Mays, Major Professor

We have read this thesis and recommend its acceptance:

Bin Zhao, Janice Musfeldt

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Xiao Ma entitled "Free Radical Polymerization in Room Temperature Ionic Liquids." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Jimmy W. Mays

Major Professor

We have read this thesis
and recommend its acceptance:

Bin Zhao

Janice Musfeldt

Accepted for the Council:

Anne Mayhew

Vice Chancellor and Dean of Graduate Studies

(Original signatures are on file with official student records.)

FREE RADICAL POLYMERIZATION IN ROOM TEMERATURE IONIC LIQUIDS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Xiao Ma

August 2006

Dedication

This dissertation is dedicated to my beloved mother. It is also dedicated to all the people who encourage, inspire and support me to achieve my goal.

Acknowledgements

I wish to thank all those who helped me complete my Master of Science degree in Chemistry. I would like to thank my principle advisor: Prof. Jimmy W. Mays for his guidance and effort in introducing me to the field of room temperature ionic liquids. I would like to thank both Dr. Bin Zhao and Dr. Janice Musfeldt for serving on my committee. I would also like to thank Dr. Hongwei Zhang for leading me to the field of room temperature ionic liquids, and Dr. Tianzi Huang for his kind help and support throughout the research process. I am also indebted to all my colleagues in Dr. Mays' group for their generous help on both research work and daily life.

Finally, I would like to thank my family and friends, whose encouragement and support made this work possible.

Abstract

The methodology of conventional free radical polymerization was employed throughout our research to study polymerization behavior in three RTILs (room temperature ionic liquids): 1-butyl-3-methylimidazolium hexafluoroposphate ([BMIM]PF_6), (tetrabutylammonium dioctyl) sulfosuccinate (Terrasail) and (1-isopropyl-3-methylimidazolium) methanesulfonate (Marisail).

Sequential addition free radical polymerization in RTILs emerged as a new route to obtain polystyrene - poly(methyl methacrylate) block copolymers. We applied the same strategy to the block copolymerization of other two systems: the monomer pair of styrene-vinyl acetate in Terrasail, and the monomer pair of styrene-acrylic acid in [BMIM]PF_6. While styrene-vinyl acetate block copolymers with a composition of 50% (VAc mol%) were obtained, the polymerization of styrene-acrylic acid only yielded polymers with mainly styrene units. Therefore, sequential addition free radical polymerization in RTILs is not effective on all polymerization systems (eg. Styrene-acrylic acid/[BMIM]PF_6).

Our study on free radical homopolymerization of 2-hydroxyethyl methacrylate (HEMA) in RTILs showed that the positive effects of employing RTILs as reaction medium could be extended from polymerization of alkyl methacrylates to that of functional methacrylates. All of the reactions exhibited very high polymerization rates, and the resulting products possessed higher molecular weight than those polymers obtained using methanol as solvent.

Copolymerizations of the monomer pairs styrene/vinyl acetate, styrene/acrylic acid, styrene/HEMA (2-hydroxyethyl methacrylate) were carried out in RTILs via

conventional free radical polymerization. However, our results failed to show any dramatic effects of RTILs on the free radical copolymerization, although RTILs are believed to be able to enhance the rates of propagation while depressing the rates of termination in homopolymerizations.

Table of Contents

List of Tables

List of Figures

1 Introduction

1.1 General Introduction to Room Temperature Ionic Liquids

Room temperature ionic liquids have become promising candidates to replace traditional molecular solvents in both the chemical industry and in academia because of their ease of handling, low vapor pressure, and the potential for recycling.

Room temperature ionic liquids are also called molten salts and are liquids containing only cations and anions at ambient temperature. Since the first report of a room temperature ionic liquid (RTIL), $[EtNH_3][NO_3]$ in 1914[1], a great deal of research effort has been exerted to exploit the possible applications of RTILs. Their weakly coordinating anions, e.g. BF_4^- and PF_6^- make them highly polar yet non-coordinating solvents. Their hydrophilicity/lipophilicity is adjustable by varying the combination of cations and anions, and thus RTILs are also referred to as "designer solvents". They exhibit a relatively wide electronchemical window, good electronic and ionic conductivity, a broad range of room temperature liquid compositions and excellent chemical, thermal, air and moisture stability[2-8].

Recently, the lack of volatility in room temperature ionic liquids, a unique property that has been assumed to be common to all ionic liquids that do not undergo thermal decomposition, is being challenged. Earle[9] and colleagues discovered that certain ionic-liquid structures known for their very high thermal stability, in particular bis{(trifluoromethyl)sulphonyl}amide salts, can be evaporated and re-condensed under relatively mild conditions. This discovery facilitates application of ionic liquids in some fields such as gas-phase processes.

One blooming application of RTILs is as the reaction medium in organometallic catalysis, due to the fact that most RTILs have limited miscibility with some common organic solvents but high compatibility with transition metals. Therefore, a so-called liquid-liquid biphasic catalysis ("biphasic catalysis") concept could be applied to RTIL/organic solvent biphasic systems, in which a homogeneous catalyst is immobilized in the RTIL phase while the reactants and/or products reside largely in the organic solvent phase[10]. These biphasic systems combine the advantages of both homogeneous (greater catalyst efficiency and mild reaction conditions) and heterogeneous (ease of catalyst recycling and separation of the products) catalysis, and thus various common organic reactions employing organometallic catalyst have been tried in different ionic liquids as alternative reaction media including hydrogenations[11], dimerizations and telomerizations[12, 13], hydroformylation[14], alkoxy carbonylation[15], alcohol oxidations[16], Heck coupling reactions[17], Suzuki couplings[18-20], Sonogashira couplings[21, 22], Stille couplings[23], Ullmann couplings[24], alkylations[25], ring-closing olefin methathesis reactions[26, 27], Diels-Alder reactions[28], Friedel-Crafts reactions[29], and nucleophilic substitutions[30].

1.2 Application of Ionic Liquids in Polymer Systems

1.2.1 Polymerization in Ionic Liquids

As described above, although ionic liquids have been already widely investigated in synthesis of low molecular organic compounds, their use in polymer synthesis is still in its infancy. One of the earliest examples of polymerization in RTILs was reported in 1990[31]. Carlin and coworkers carried out Ziegler-Natta polymerization of ethylene

using $TiCl_4$/AlEthylCl_2 catalysts in a Lewis acidic ionic liquid: $AlCl_3$-1-ethyl-3-methylimidazolium Chloride [EMIM]Cl. Although the yield of polyethylene (PE) was low, the $TiCl_4$ catalyst precursor was still able to promote polymerization with a catalytic activity up to 0.023 g of ethylene min^{-1} due to the acidic nature of EMIM]Cl. Later, the same group[32] reported that high yields of PE could be achieved in a similar RTIL system by replacing $TiCl_4$ with Cp_2MCl_2 (Cyclopentadienyl dichloride complexes of M; M=Ti, Zr, and Hf). Nevertheless, these works have opened a new route to synthesize polymers using RTILs as alternative reaction media. At the very beginning, the use of ionic liquids was mainly as convenient electrolytes[33], however Carlin and Osteryoung[34] produced a new electroactive material by electrochemical oxidation of triphenylsilyl chloride (Ph_3SiCl) in the acidic ionic liquid ($AlCl_3$-[EMIM]Cl). The obtained film was self-standing, flexible, and exhibited high ionic conductivity as well as rubbery gel electrolyte properties. However, most of the RTILs employed in the above works are the 1st generation ionic liquids, which are chloroaluminate based ionic liquids and have quite high moisture sensitivity and the decomposition product of hydrolysis, HCl, is highly corrosive. Not much polymerization work was done in these moisture-sensitive ionic liquids although there are certain advantages of polymerization in RTILs compared to traditional solvents, until the introduction of 2nd generation of air, moisture and thermally stable neutral ionic liquids, composed of dialkylimidazolium cations and PF_6 or BP_4 anions.

1.2.2 Free Radical Polymerization

Free radical polymerization involves long chain free radicals as propagating species, usually initiated by the attack of free radicals derived by thermal or photo-chemical

decomposition of initiators. Polymerization proceeds by the chain reaction addition of free radical chain ends to double bonds of monomer molecules. Finally two propagating species (growing free radicals) combine or disproportionate to terminate the chain growth. Because of its versatility, synthetic ease, compatibility with a wide variety of functional groups, and its tolerance to water and protic media, free radical polymerization has been widely used in industry and in academia for the synthesis of various polymeric materials. However, typical free radical polymerization has a significant drawback, in that these polymerizations proceed with accompanying chain-breaking reactions due to the radical character of propagating centers. Bimolecular termination and chain transfer are ever present in radical chain polymerization and limit the lifetime of the propagating radicals. The polymers obtained are therefore polydisperse with very limited control over macromolecular weight and architecture. In “living polymerization” techniques, in which the termination is greatly diminished, much of the academic and industrial research of earlier years has focused on anionic, cationic, coordination, and ring-opening polymerizations. Although these methods can generate polymers with low polydispersity, controlled molecular weight, and defined chain ends and architecture, they are not suitable for the polymerization and copolymerization of a wide range of functionalized vinylic monomers. Take anionic and cationic techniques for example. The incompatibility of the growing polymer chain end (carbanion or carbocation) with numerous functional groups and certain monomer families limits their use in both industry and academia. Furthermore, the moisture and oxygen sensitive nature of the propagating species, stringent reaction conditions, including the use of ultrapure reagents and the need for rigorous exclusion of water and oxygen, prevents the widespread use of

these techniques. This limitation inspired the search for new polymerization concepts and thus the discovery and development of living free radical polymerization. The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant than ionic polymerizations of functional groups and impurities and is thus the leading industrial method to produce polymers. All of the newly emerged CPR methods are based on establishing a rapid dynamic equilibrium between the growing free radicals and dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters, as in reversible addition fragmentation chain transfer processes (RAFT), alkoxyamines, as in nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP), and potentially even organometallic species.[35] Specifically, the general mechanism of these processes is the reversible termination of the growing polymeric chain with the mediating radical to reduce the overall concentration of the propagating radical chain ends. In the absence of the other reactions leading to initiation of new polymer chains (i.e., no reaction of the mediating radical with the vinylic monomer), the concentration of reactive chain ends is extremely low, minimizing irreversible termination reactions, such as combination or disproportionation. All chains would be initiated only from the desired initiating species and growth should occur in a living fashion, allowing a high degree of control over the entire polymerization process with well-defined polymers being obtained.[36, 37]

Solution polymerization is currently widely used in industry due to the fact that during polymerization of a monomer in a solvent, the solvent acts as diluent and aids in the transfer of the heat of polymerization. However, this approach has limitations as the

rate of reaction is decreased, and as volatile organic compounds (VOCs) are emitted into the environment[38]. With the introduction of 2nd generation of air, moisture and thermally stable neutral ionic liquids, polymer chemists realized that RTILs could be promising reaction media for polymerizations. Despite the fact that these ionic liquids are assumed to be potential solvents for ionic polymerization due to their highly polar nature, the first report of polymerization in the new non-hydroscopic ionic liquids was based on a free radical polymerization process – atom transfer radical polymerization (ATRP). Carmichael et al.[39] reported in 2000 that the reactions progressed in a manner consistent with a living polymerization over a wide range of reaction temperatures using ethyl-2-bromoisobutyrate initiator and CuBr/N-propyl-2-pyridylmethanimine as the catalyst pair in 50/50 (V/V) MMA/[BMIM]PF_6 system. First-order kinetic behavior and evolution of number-average molecular weight (M_n) with time were observed. Faster polymerization rates were observed as compared to those in common solvents while the polydispersities were narrow: 1.30~1.43. The final product was separated from solution (PMMA and catalyst are miscible with [BMIM]PF_6) by extraction with toluene, while copper catalyst remained in the ionic liquid phase, which facilitated the catalyst re-use by adding fresh monomer and also excluded the need for post purification procedure by passing the solution through purification columns to remove the toxic copper salt.

Although the mechanisms have not been fully understood, two features of ionic liquids, high polarity and high viscosity, are considered to be the causes of the higher polymerization rates than those in common solvents. Carmichael et al. attributed the polymerization behavior they observed to the increased polarity of ionic liquids because a similar increase in the rate has been observed with other polar/coordinating solvents,

while Hong et al.[40] discussed the viscosity feature. Their work [40] showed large increases in both the rate of polymerization and the molecular weights that were obtained in the polymerization of methyl methacrylate (MMA) in [BMIM]PF_6 as compared to those in conventional organic solvents. They believed these dramatic increases were at least in part because of the high viscosity of the polymerization media, and thus proposed a "diffusion-controlled termination" mechanism to explain the diminished chain terminations in viscous system. Harrison et al.[41, 42] measured the rate constant of the propagation (k_p) by using a pulsed laser polymerization (PLP) technique to polymerize MMA in [BMIM]PF_6, which is the IUPAC-recommended standard procedure. They found that both an increase of k_p and decrease of k_t contribute to a roughly 10-fold increase of over-all rate of polymerization, which were significantly affected by [BMIM]PF_6. They attributed the increase of the propagation rate to the increased polarity of the ionic liquid solution, which lowers the activation energy of propagation through charge-transfer interactions. On the other hand, the termination rate is decreased simply because of the increased viscosity of the polymerization medium. Attempts to correlate viscosity of RTILs with polymerization data have also been made. Strehmel et al.[43] found that the higher the viscosity, the higher yields and molecular weights of the polymers while Zhang et al.[44] reported that physical data with polymerization behaviors in RTILs revealed that no obvious trend existed between polarity or viscosity of RTILs and polymerization rate or molecular weight of the formed polymer. The discrepancy may arise from two factors. Firstly, Zhang tried to keep monomer conversions low enough to avoid the Trommsdorff effect while Strehmel carried their polymerizations to high conversions, where the Trommsdorff effect impacts

polymerization because the high viscosity will affect polymerization behavior in this regime. Secondly, the RTILs employed in Stremel's case are actually composed of cations and anions of similar structures except for the variation in the alkyl length and positions on the cation, while either cations or anions are structurally different in Zhang's case. Thus, Zhang stated that it was still too early to make a conclusion that polarity or viscosity has no apparent effect on the MMA in RTILs. The polarity of molecular solvents is complex, involving many interactions including: H-bonding, p-interaction or van der Waals forces. In RTILs, polarity is more complicated since both cations and anions may have their own distinct interactions. In addition, the polymers synthesized in RTILs have similar glass transition temperatures and local microstructures as those obtained in benzene or bulk, as analyzed by thermoanalysis techniques and ^{13}C-NMR spectroscopy[45, 46].

Recently, Strehmel et al.[43] extended their research to free radical polymerization of n-butyl methacrylate initiated by AIBN into a wider range of ionic liquids, which were based on imidazolium, pyridinium, and alkylammonium salts. The reactions were carried out under nitrogen atmosphere at 70^{o}C for as long as 24 hrs. They observed a widespread phenomenon for ionic liquids of different cation and anion structure. That is, the use of ionic liquids results in higher molar masses of the polymers, which can exceed even the molar masses obtained by bulk polymerization notably, and consequently, the increased glass transition temperature of the polymers together with a reduction in their thermal degradation in comparison with the polymer made by solution polymerization in toluene. They also discovered that imidazolium based ionic liquids were preferable over *n*-alkyl-4- methylpyridinium and aliphatic ammonium salts because of higher degree of

polymerization of the poly(butyl methacrylate)s obtained in the imidazolium salts. Though polymerization in ionic liquids was initially considered as "green chemistry" due to the presumed nonvolatile natural of RTILs, before long chemists realized the necessity of using volatile organic compounds (VOCs) during the recovery of final products from RTILs. Thus, in order to make the process more environmentally friendly, Guerrero-Sanchez et al.[38] studied ionic liquids as solvents in water-soluble systems. The principles involved taking advantage of the miscibility of some RTILs with water and the insolubility of several important commercial polymers in this natural solvent, as an alternative for the separation process. Among the advantages of this alternative approach are: the saving of resources (since RTILs can be reused and the polymerization reactions can be performed at lower temperature than normally required) and the minimum emission of VOCs into the environment. Methyl methacrylate (MMA), butyl methacrylate (BMA) and styrene (St) were polymerized in two RTILs, 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM]BF_4) and 1-ethyl-3-methyl-imidazolium tosylate ([EMIM]TOS), using 2,2′-azobisisobutyronitrile (AIBN) as initiator. Preliminary results showed MMA and BMA conversions reached over 80% in less than an hour, and thus demonstrated the feasibility to use water soluble RTILs efficiently as reaction media. In addition, a concept of continuous industrial production of PMMA with the use of water soluble RTILs was proposed.

Besides commonly used thermal decomposition initiation, other initiation methods such as radiation initiation have been tried in RTILs. Liu[47, 48] carried out polymerization of St, MMA and butyl methacrylate (BMA) in a RTIL $[Me_3NC_2H_4OH]^+[ZnCl_3]^-$ and its mixture with THF initiated by ^{60}Co gamma radiation.

Their work suggested that radiation polymerization in ionic liquids followed a radical propagating process. Free radical copolymerizations in ionic liquids were reported as well.[49, 50]

As discussed above, atom transfer radical polymerization has attracted great interest in the field of polymer synthesis. However, a potential limitation to commercialization of this technology is that relatively high levels of catalyst and ligand are often required in order to obtain an acceptable reaction rate[51, 52]. Thereafter, the removal and the recycling of catalytic materials are necessary. To overcome this problem, it is expected that using ionic liquids as polymerization solvents will make the removal and the recycling of the catalytic materials easier because of their good dissolving power for transition metals. Biedron et al.[53] described a now-called "biphasic" ATRP in [BMIM]PF_6. Depending on the solubilities of alkyl-substituted acrylates (methyl, butyl, hexyl or dodecyl) in the RTILs, polymerization may proceed either homogeneously or heterogeneously. A heterogeneous system was formed for the alkyl acrylate, which is not completely soluble in the RTILs, and thus formed an upper monomer phase while CuBr/pentamethyldiethylenetriamine (PMDETA) catalyst remained in the lower RTIL phase. Methyl acrylate (MA) and poly(methyl acrylate) (PMA) are miscible with [BMIM]PF_6 and form a homogeneous polymerization system, therefore, all reactions proceed in one phase. For other acrylates, the growing macromolecular chains react with the monomer at the interface but reside predominantly in the monomer phase. Ding[54] reported an ionic liquid catalyst, synthesized by anchoring CuBr/N,N,N",N"-tetraethyldiethylenetriamine (TEDETA) on an imidazolium-based ionic liquid (BITT), for biphasic ATRP of MMA. The required ionic liquid was only 5 wt% of the organic

solvent. The polymerization was well controlled, producing polymers with high initiator efficiency and low polydispersity (approximately 1.2-1.4). The liquid catalyst could be easily isolated from the polymer solution and the recycled catalyst retained high activity.

Sarbu et al.[55] successfully carried out ATRP in a range of 1-butyl-3-methylimidazolium ionic liquids by using different catalyst systems (iron or copper halide). They found that in iron-mediated ATRP, no additional ligand was required to achieve a controlled polymerization of MMA, although both of reaction and initiation rates were low. On the contrary, maintaining controlled polymerization natural without using organic ligands can only be achieved in a phosphonate ionic liquid for copper mediated ATRP of MMA, while a ligand was required in ionic liquids with halide or carbonate anions.

Biedron[53] conducted ATRP of methyl acrylate and ethyl acrylate in a chiral ionic liquid containing a center of chirality in a cationic fragment: ethyl L-lactate tosylate. However, their results showed that the chiral natural of this ionic liquid had no significant effect on the stereochemistry of polymer chain propagation.

Generally, ATRP in ionic liquids proceeds with low initiation efficiency. This has been attributed to the high concentration of the catalyst in the RTIL phase, into which the small initiators can easily diffuse and thus generate high concentration of free radicals. The free radicals can easily undergo irreversible termination and cause the low initiation efficiency. However, this situation can be improved by employing macroinitiators, which have low diffusion coefficient to the RTIL phase. In addition, the catalyst can be regenerated after removal of polymer and unreacted monomer.

Reversible atom transfer radical polymerization of MMA in [BMIM]PF_6,

[BMIM]BF_4 and [DMIM]BF_4 (1-dodecyl-3-methylimidazolium tetrafluoroborate) have been reported[56, 57]. In [BMIM]PF_6, the (AIBN)/$CuCl_2$/2,2'-bipyridine initiation system was introduced, and the reaction proceeded in a homogeneous way. Due to a cage effect with ionic liquid molecules, the termination of the primary radicals through decomposition of AIBN might occur before they can initiate polymerization, which accounts for the low initiation efficiency of AIBN. Due to the good solubility of Cu catalyst in the ionic liquid, less catalyst is needed to effectively mediate the polymerization process in ionic liquids that in other ATRPs. The ionic liquids and catalyst can be recovered and reused.

Nitroxide-mediated radical polymerization has been tried in ionic liquids as well. Zhang et al.[58] employed both a bimolecular initiator system (benzoyl peroxide (BPO) + 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)) and a universal initiator system (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TMPPAH)) for the attempted nitroxide-mediated polymerization of MMA and St in an ionic liquid: 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6). However, because of the low rates of the mediating radical and slow degradation of free TEMPO at the elevated temperatures in the presence of [BMIM]PF_6, the polymerizations were not living/controlled for either monomers. Ryan et al.[59] achieved a controlled/living polymerization of MA in 50% V/V of [HMIM]PF_6 initiated by the initiation pair: AIBN+4-oxo-2,2,6,6-tetramethyl-1-piperidine-N-oxyl (4-oxo-TEMPO) at 140^{o}C-155 ^{o}C. The reaction rates were greater than in anisole, and were similar to the rate of spontaneous polymerization in the ionic liquid. In both works, self-polymerizations were observed because of the high temperature used. Other kinds of living free radical

polymerization such as RAFT and charge transfer polymerization have also been reported[60-62].

Copolymerization of N-hexylmaleimide and styrene via ATRP has been conducted in [BMIM]PF_6.[63] The two monomers tended to form alternating structure in RTILs, which differed from those conducted in anisole. It is shown that combining catalyst CuBr/PMDETA with dendritic polyacrylether 2-bromoisobutyrates (Gn-Br, n=1-3) could yield an effective macroinitiators for ATRP of N-hexylmaleimide and styrene in [BMIM]PF_6 at lower temperature than that in anisole. The polymerizations were well-controlled and low polydispersity products were obtained (1.18<PDI<1.36).

Furthermore, attempts to synthesize block copolymers in RTILs have been made. Zhang et al.[64] demonstrated the formation of PS-b-PMMA by sequential addition in [BMIM]PF_6 through the traditional free radical polymerization mechanism using benzoyl peroxide (BPO) as initiator. St was polymerized first and then was gradually precipitated out when the conversion reached around 50% due to the insolubility of PS in [BMIM]PF_6. After adding the second monomer (MMA), diblock copolymers were formed at room temperature. The key to the success was that the chain coils wrapped the PS macro-radicals inside resulting in prolonged lifetimes because of the diminished termination. However, reversed and sequential addition polymerization only afforded homopolymer PMMA. Different results arose from the differences in monomer solubilities of St and MMA in [BMIM]PF_6. Zhang and coworkers also experimentally studied the solvent effect on reactivity ratios and sequence length distributions for free radical polymerization. The calculated reactivity ratios of St and MMA (r_{st} = 0.381 ± 0.02 and r_{mma} = 0.464 ± 0.02) in [BMIM]PF_6 by non-linear method (CONTOUR computer

program) were significantly different from those (r_{st}=0.54±0.04 and r_{mma}=0.50±0.04) in benzene at 60^{o}C[65]. The "boot-strap" model[66], polarity of the solvents, interaction between solvent and monomers (e.g. solvent-monomer complex), viscosity and system heterogeneity all possibly contribute to the apparent difference of the reactivity ratios in RTILs and in benzene.

Living radical polymerization has been employed to make block copolymers in RTILs as well. Kubisa and coworkers produced PBA1-b-PMA2 and PMA1-b-PBA2 with different sequence of addition of monomers by ATRP method in [BMIM]PF_6[53]. They found that when conversion of MA, the first polymerized monomer exceeded 70%, a significant percentage of PMA chains would be "dead", and thus became homopolymer. However, for the reverse polymerization order, "clean" diblock can be formed essentially free of either BA or MA homopolymer. (Even BA can be polymerized to complete conversion.) Ma et al.[56, 57] described a successful strategy of synthesis of block copolymer, in which St was reinitiated by chlorine-atom-ended PMMA macroinitiators via reverse ATRP in [BMIM]PF_6, [BMIM]BF_4 and [C_{12}MIM]BF_4 (1-dodecyl-3-methylimidazolium tetrafluoroborate).

1.2.3 Ring-opening Polymerization

Ring-opening polymerization (ROP) is of importance with cyclic monomers such as cyclic ethers, acetals, amides (lactams), esters (lactones), and siloxanes. RTILs have been applied in the field of ROP. By using cationic allenylidene precatalyst: [(p-cymene)RuCl(Pcy_3)(=C=C=CPh_2)][OTf], Csihony[67] carried out ring-opening metathesis polymerization of norbornene in a biphasic medium (1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BDMIM]PF_6/toluene), in which the catalyst

remained in the ionic liquid phase while the upper toluene phase dissolved the formed polymer. Besides the ease of separating polymer from catalyst, both the ionic liquid and catalyst can be reused up to six times without significant loss of catalytic activity and led to quantitative yields of polymer. After reloading of catalyst, the catalyst system can still be used for up to five times.

Biedron et al.[53] attempted cationic ring opening polymerization of 3-ethyl-3-hydroxymethyloxetane in the most common hydrophilic ionic liquid: [BMIM]BF_4 using BF_3-Et_2O initiation system. The relatively high polarity of ionic liquids considerably reduced the intermolecular H-bonding leading to the formation of aggregates, whereas the intramolecular H-bonding facilitating intramolecular chain transfer is not significantly affected. The multihydroxyl, branched structure was preserved, and the molecular weights of polymers were in the same range as those made in organic solvents or in bulk. In the same ionic liquid, Xiong[68] conducted ring-opening polymerization of ε-caprolactone (ε-Cl) using $LnCl_3$/epoxides as catalyst. High conversion (96.0%) was observed under mild reaction condition (60^{o}C, 30 min).

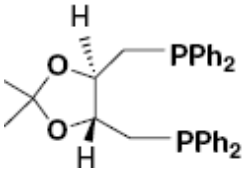
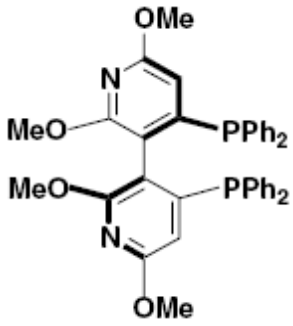
The application of ionic liquids can also help to reduce the reaction temperature. Polycarbonate made by ring opening polymerization of ethylene carbonate may undergo decarboxylation when reaction is carried out at 180-200°C[69]. In acidic ionic liquids such as [BMIM]Cl-$AlCl_3$ or [BMIM]Cl-$SnCl_2$, however, the reaction can take place at temperature below 100°C or at 120°C depending on the ionic liquid used, leading to a decrease of the decarboxylation side reaction, although low content of ethylene carbonate polymer was formed.

1.2.4 Electrochemical Polymerization

During electrochemical polymerization, polymer is formed when current is passed through a solution resulting in oxidation (electron loss) at the anode and reduction (electron gain) at the cathode. Due to some advantages over chemical synthesis including faster reaction, simple procedure, generation of the polymer in the doped state and easy control of the film thickness, electrochemical polymerization became the main method to synthesize conducting polymer for potential application in energy storage devices, electrochromic devices and light-emitting diodes. Naudin et al.[70] reported electrochemical polymerization of poly(3-(4-fluorophenyl)thiophene) (PFPT) in ionic liquids. The electrochemical behavior was similar to that in common non-aqueous electrolyte. However, X-ray photoluminescence spectroscopy revealed some ionic liquid residue in the formed film. Other kinds of conjugated polymers such as polypyrrole and polyaniline were also synthesized in ionic liquid[71, 72]. Poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesized by electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) using imidazolium and pyrrolidinium-based TFSA [trifluoromethanesulfonylamide] ionic liquids as both the growth medium and the electrolyte.[73]

1.2.5 Transition-metal Catalyzed Polymerization

Insertion polymerizations of vinyl monomers are typically catalyzed by cationic metal complexes with weakly coordinating anions. Polar, non-coordinating RTILs are attractive solvents for these reactions, since they may stabilize the solvent separated ion pairs that are necessary for high activity. Rogers and coworkers[74] have used 1-hexylpyridinium bis(trifluoromethanesulfonyl) imide ($[C_6Pyr][NTf_2]$)/methanol as a solvent pair for

palladium-catalyzed alternating copolymerization of styrene and carbon monoxide. The catalyst used was $LPd(OAc)_2$ (L=2,2'-bipyridine and 1,10-phenanthroline). $[C_6Pyr][NTf_2]$ and catalyst can be recycled and the yields and molecular weights were higher as compared to the polymerization carried out in methanol alone. Furthermore, the catalyst stability and propagation rate were improved due to the inhibited chain transfer and catalyst decomposition in $[C_6Pyr][NTf_2]$. Pd-catalyzed asymmetric alternating co-polymerization has been carried out in ionic liquids as well: Wang[75] synthesized regioregular polyketones from propene and carbon monoxide using chiral ligands, such as (2S,3S)-DIOP () and (R)-P-Phos () in $[BMIM]PF_6$ or $[BMIM]PF_6$ as a reaction medium. It showed that with (2S,3S)-DIOP as chiral ligand and $[BMIM]PF_6$ as medium, the Pd-catalyzed co-polymerization of propene and CO gave almost completely regioregular polyketones, whereas the highest molar optical rotation = +15.9 and polydispersity = 1.2 were attained when (R)-P-Phos was used as the ligand and $[BMIM]PF_6$ as the solvent. The copolymer exhibited regioregularity of H-H/H-T/T-T (%) = 17:66:17.

Poly(phenyl-acetylene) (PPA) is a conjugated polymer with interesting photoconductivity, photoluminescence, non-linear optical properties and membrane properties. It can be obtained by different polymerization methods including radical, cationic, metathesis catalyst or Ziegler-Natta polymerization. High molecular weight

PPA can also be obtained by Rh(I) catalyzed phenylacetylene polymerization in ionic liquids such as n-butylpyridium tetrafluoroborate ([bupy]BF_4) or [BMIM]PF_6[76]. The catalyst used was either (diene)Rh(acac) or [(diene)RhCl2]2, and the cocatalyst used was triethylamine. The polymer was separated from the ionic liquid using either extraction with toluene or filtration by adding methanol into ionic liquid to form a suspension of PPA in the solvent mixture methanol/RTIL. Extraction usually facilitates the catalyst recycling, but cannot permit the maximum product recovery. While more polymer can be recovered through the filtration method, the Rh(I) complex solution after filtration shows no catalytic activity. The molecular weights were from 55,000 to 200,000.

1.2.6 Polymerization of Ionic Liquids

The polymer forms of ionic liquids have been found to be potential new polymer materials with exceptional properties, due to their stability, electrochemical activity, and CO_2 absorption ability. Ohno and coworkers[77-80]synthesized poly(ionic liquid)s by free radical polymerization and obtained flexible and transparent films with excellent ionic conductivity from their polymer brushes and crosslinked polymers. Shen and coworkers[81] observed that the CO_2 absorption of poly(ionic liquid)s, 1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate polymer (PVBIT) and 1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate polymer (PVBIH), both of which was synthesized by free radical polymerization, was much faster than that of room temperature ionic liquids. The same group[82] reported a well controlled ATRP of the previous two ionic liquids by using CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine or CuBr/2,2'-bipyridine as the catalyst and ethyl 2-bromoisobutyrate as the initiator.

1.3 General Introduction to Polymerization of HEMA

HEMA (2-hydroxyethyl methacrylate) homopolymer is a typical hydrophilic polymer and has a high degree of hydration, however, it is not water-soluble.[75] Synthesis of poly(HEMA) and its copolymers is of great interest because of their wide variety of applications. Their biocompatibility makes them excellent candidates for the preparation of various biomedical and pharmaceutical materials like optical lenses, implants, drug delivery devices, and polymeric supports for enzyme immobilization.[83, 84]

Anionic polymerization has long been adopted to synthesize controlled structure HEMA homopolymer or HEMA-based block copolymers,[85] but this approach requires protection of the alcohol functionality due to the labile proton on the hydroxyl group.[86] Thus obvious drawbacks include the cumbersome protection and deprotection procedures and low reaction temperatures needed for living anionic polymerization of methacrylates.[87]

Recent years have witnessed the emergence of living radical polymerizations and because of its great versatility with a wide range of monomers, the control of the molecular weights, and the low polydispersities of the resulting polymers. Synthesis of poly(HEMA) via this method is of particular interest, in that the protection of functional group is not necessary and the reaction conditions are less strict. The efficient, controlled polymerization of HEMA was achieved by Armes et al.[75] using ATRP in methanol/ water mixtures or in methanol (M_w/M_n=1.2-1.3).

2 Experimental

2.1 Materials

HEMA, acrylic acid, VAc and St (Aldrich, 99%) were distilled under vacuum just before use. Benzoyl peroxide (BPO) (Aldrich, 97%) was recrystallized from chloroform. [BMIM]PF_6 (1-butyl-3-methyl- imidazolium hexafluorophosphate) (Sachem) was washed by distilled water for 10 times and dried under vacuum over night. Terrasail and Marisail (Sachem) were dried under vacuum over night prior to use. All other organic solvents (Aldrich, 99%) were used as received.

2.2 Instrumentation

The size exclusion chromatography (SEC) experiments were carried out at 30 °C using a Polymer Laboratories Knauer 501 HPLC pump and Knauer 2301 RI detector. Two PSS (Polymer Standard Service) columns were used (one 100Å pore size and one linear mixed bed column). The flow rate of the mobile phase (tetrahydrofuran, THF) was 1 mL/min. The ^{1}H and ^{13}C spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer using $CDCl_3$, $(CD_3)_2SO$ or $DCON(CD_3)_2$ as solvents and internal references. Differential Scanning Calorimetry (DSC) was carried out on a DSC Q1000 (TA Instruments) in the Polymer Characterization Laboratory at the Chemistry Department (University of Tennessee at Knoxville) under nitrogen using (scanning rate 10°C min^{-1}). Polarity tests were run on a Perkin-Elmer Instruments, Lamda 35 UV/Vis Spectrometer (Perkin-Elmer). Transition energy, E, of the solvatochromic band, was calculated by equation: $E=28591.44/\lambda_{max}$ in kcal/mol or $=(hcN_A/lmax)\times106$ (h is Planck's constant, c is the speed of light, N_A is Avogadro's number and lmax is the wavelength of

maximum absorption; 1 cal is 4.184 J). Viscosities were measured by AERS-LS #0012005 rheometer (Rheometric Scientific (TA Instruments)): Angular velocity: 7.0498 (rad/s).

2.3 Polymerizations

2.3.1 Homopolymerization and Copolymerization

All polymerizations were performed under a dry nitrogen atmosphere. The initiator, monomer or monomer pairs and reaction media were weighed and measured into flasks separately. After bubbled by dry nitrogen for 30 minutes, the flasks were kept in a water bath at 70℃ for a certain time. The polymerizations were stopped by precipitation into appropriate organic solvents. After the decantation of solvent, the crude polymer was dissolved in THF and re-precipitated repeatedly, then dried under vacuum to constant weight. Conversions were determined gravimetrically.

2.3.2 Sequential Block Copolymerization

First monomer was polymerized in a certain ionic liquid for 4 h at 70 ℃ using BPO as initiator. Then predetermined amount of second monomer was introduced via vacuum followed by heat-sealing the reactor from the vacuum line and the reaction was allowed to proceed for 4 days in room temperature. To stop the reaction, the mixture was precipitated in appropriate solvent. The crude polymer was dissolved in THF and reprecipitated for three times, and then was dried for further characterization. Methanol (for PVAc or PAA) and cyclohexane (for PS) was used to Soxhlet extract any homopolymers.

3 Results and Discussion

3.1 Solubility Tests

The success of block copolymer formation in this work was thought to depend on the poor solubility of the first polymer chains in the ionic liquids. The precipitation of the first block from the medium under the reaction temperature hinders diffusion of the propagating radical centers, which must find one another to terminate, and thus increases their life times.[88] When the second monomer which is soluble with the reaction medium at room temperature is added, it diffuses to the radical sites, polymerization continues and block copolymer is formed.[64] Therefore, solubility tests of monomers and their polymers under both the reaction temperature (70^{o}C) and the room temperature were conducted. Tests were carried out by adding 1 ml monomer into 1 ml RTIL under room temperature, as shown in **Table B-1** or 70°C, shown in **Table B-2**, and allowing the mixture to stand overnight.

[BMIM] PF_6 (1-butyl-3-methylimidazolium hexaflurophosphophate **Figure A-1**) is probably the most commonly studied ionic liquid, and [BMIM] BF_4 (1-butyl-3-methylimidazolium tetrafluroborate **Figure A-2**) is another commonly used imidazolium RTIL. Terrasail (**Figure A-3**) is the viscous hydrophobic RTIL (tetrabutylammonium dioctyl) sulfosuccinate, whereas Marisail (**Figure A-4**) is a hydrophilic and less viscous RTIL (1-isopropyl-3-methylimidazolium) methanesulfonate. At least one of the RTILs was found to serve as a solvent for each of the monomers studied, while many of the polymers were insoluble in all of the RTILs tested. Terrasail was found to dissolve the most monomers and polymers among those tested, while Marisail dissolved the fewest

Table B-1 Solubility tests at room temperature

	[BMIM][BF_4]	[BMIM][PF_6]	Terrasail	Marisail
tert-Butylacrylate	N	Partial	Y	N
PtBA	N	N	N	N
Acrylic acid	P	Y	Y	Y
PAA	N	N	N	N
t-BMA	N	N	Y	N
Pt-BMA	N	N	N	N
DEAEMA	N	N	Y	N
Poly (DEAEMA)	N	N	Y	N
DMAEMA	N	Partial	Y	N
Poly(DMAEMA)	N	N	Y	N
vinyl pyrrolidone	Y	Y	Y	Partial
PVP	N	N	N	Y
Vinyl acetate	N	Y	Y	N
PVAc	N	N	N	N
4-vinyl pyridine	Y	Y	N	N
P (4-vinyl pyridine)	N	N	N	N
Acrylonitrile	C	Y	Y	Y
Poly(Acrylonitrile)	N	N	N	N
Methylmethacrylate	Partial	Y	Y	N
PMMA	N	Y	N	N
Butyl acrylate	N	Y	Y	N
PBA	Partial	N	Y	N
Styrene	N	Y	Y	N
PS	N	N	N	N
HydroxyethylMA	Y	Y	Y	Y
Poly (HEMA)	N	Partial	Y	Y

[a]Y-soluble; N-not soluble; C-crystals appeared; P-Polymer present in monomer precipitated; D-RTILs decomposed; Partial-Partially soluble.

Table B-2 Solubility tests at 70 °C

	[BMIM][BF_4]	[BMIM][PF_6]	Terrasail	Marisail
t-Butylacrylate	N	Partial	Y	N
PtBA	N	N	N	N
Acrylic acid	P	Y	Y	Y
PAA	N	N	N	N
t-MBA	N	N	Y	N
Pt-MBA	N	N	N	N
DEAEMA	N	N	Y	N
Poly (DEAEMA)	N	N	Y	N
DMAEMA	N	Partial	Y	N
Poly(DMAEMA)	N	N	Y	N
vinyl pyrrolidone	Y	Y	Y	Partial
PVP	N	N	N	Y
Vinylacetate	N	Y	Y	N
PVAc	N	D	N	N
4-vinyl pyridine	Y	Y	P	P
P (4-vinyl pyridine)	Y	N	Partial	N
Acrylonitrile	Y	Y	Y	Y
Poly(Acrylonitrile)	N	N	N	N
Methylmethacrylate	N	Y	Y	N
PMMA	N	Y	N	N
Butylacrylate	N	Y	Y	N
PBA	Y	N	Y	N
Styrene	N	Y	Y	N
PS	N	N	N	N
HydroxyethylMA	Y	Y	Y	Y
Poly (HEMA)	N	N	Y	Y

[a]Y-soluble; N-not soluble; C-crystals appeared; P-Polymer present in monomer precipitated; D-RTILs decomposed; Partial-Partially soluble.

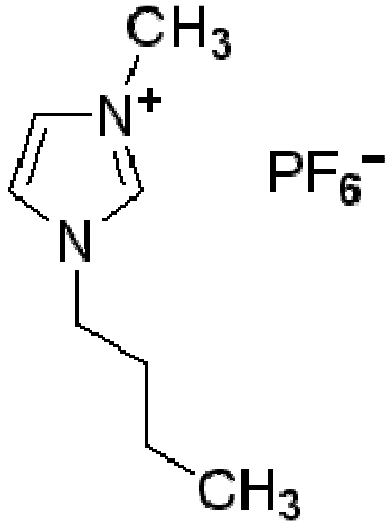


Figure A-1. Structure of [BMIM] PF_6 (1-butyl-3-methylimidazolium hexaflurophosphophate)

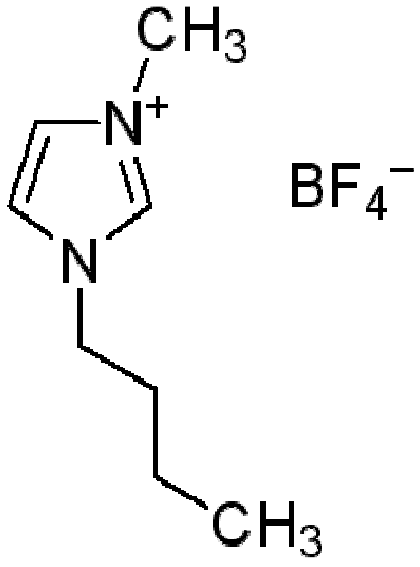
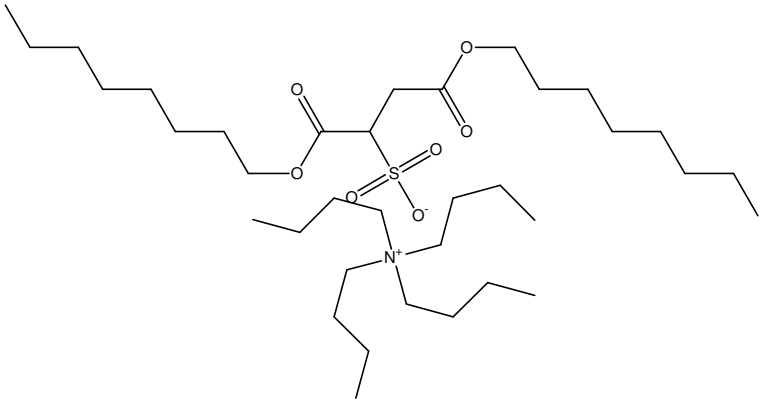
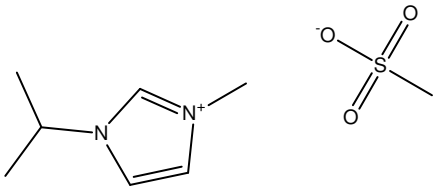


Figure A-2. Structure of [BMIM]BF_4 (1-butyl-3-methylimidazolium tetrafluroborate)



(tetrabutylammonium dioctyl) sulfosuccinate

Figure A-3. Structure of Terrasail ((tetrabutylammonium dioctyl) sulfosuccinate)



(1-isopropyl-3-methylimidazolium) methanesulfonate

Figure A-4. Structure of Marisail ((1-isopropyl-3-methylimidazolium) methanesulfonate)

monomers and polymers. Temperature (room temperature versus 70 °C) had little if any influence on solubility.

3.2 Sequential Block Copolymerization in Room Temperature Ionic Liquids

Zhang successfully obtained styrene methyl methacrylate block copolymers via sequential addition free radical polymerization in [BMIM]PF_6.[64] Thus we tried two other polymerization systems (St/VAc/Terrasail and St/AA/[BMIM]PF_6) to see whether sequential addition free radical polymerization in RTILs could be widely applied.

3.2.1 Sequential Block Copolymerization of Styrene and Vinyl Acetate

3.2.1.1 Polymerization Starting From Styrene

Terrasail was chosen to be the reaction medium in this study for the following reasons: **Table B-2** clearly showed that neither polystyrene nor poly(vinyl acetate) was miscible with Terrasail under 70 °C, while at room temperature as shown in **Table B-1**, both vinyl acetate and styrene monomer was able to be dissolved in Terrasail. Either of the two monomers could be the first polymerized monomer. Furthermore, the other hydrophobic ionic liquid - [BMIM]PF_6 - is not suitable in polymerization of vinyl acetate in that it was involved in degradation while heated with vinyl acetate, generating harmful HF gas.

Styrene was first polymerized in Terrasail for 4 h at 70 °C using BPO as initiator. About 2 ml of the mixture was sampled via a syringe under N2 atmosphere, followed by pumping off any unreacted styrene under vacuum for 3 hours. Then a predetermined

amount of vinyl acetate was introduced via vacuum distillation followed by heat-sealing the reactor from the vacuum line and the reaction was allowed to proceed for 4 days at room temperature. To stop the reaction, the mixture was precipitated in ethyl ether. The crude polymer was dissolved in THF and re-precipitated in ethyl ether three times, and then was dried for further characterization. Methanol and cyclohexane was used to Soxhlet-extract any homopolymers of poly(vinyl acetate) and polystyrene, respectively.

^{1}H NMR was utilized to characterize the final product. However, as shown in **Figure A-5**, the spectra indicate the existence of pure St units. Prior to the experiment we had believed that it would be advantageous to polymerize styrene as the first block since PS is not soluble in Terrasail. The insoluble nature of the PS radicals should increase their lifetimes (two macroradicals must diffuse together to terminate), resulting in the presence of residual PS radicals upon addition of the second monomer. Failure to obtain St-VAc block copolymers could be attributed to the large difference in relative stabilities of the two types of radicals. In another word, the PS radicals were stabilized by the benzyl rings, resulting in the lack of ability to initiate the VAc monomers. Our results indicated that Terrasail had little effect on the "stabilized" PS radicals, which was further verified by the copolymerization of St with VAc (**3.4.1**). Thus, there is not an effective crossover from styrene type radicals to vinyl acetate radicals.

Therefore, starting from styrene polymerization may not be an appropriate path to obtaining St-VAc block copolymers.

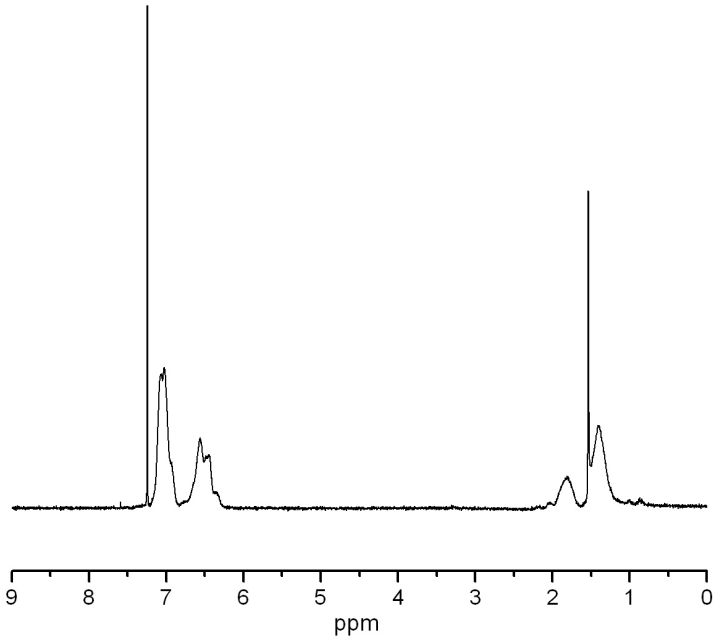


Figure A-5. ^{1}H NMR spectra of final product of sequential block copolymerization of St and VAc (starting from St)

3.2.1.2 Polymerization Starting From Vinyl Acetate

The basic approach to preparing PVAc-b-PS is as follows:

$$\text{VAc} \xrightarrow[\text{Terrasail}]{\text{BPO, } 70^{o}\text{C}} \underset{\textbf{(I)}}{\text{PVAc}^{\bullet}} + \text{VAc}$$

$$\textbf{I} + \text{Styrene} \xrightarrow{\text{room temp}} \text{PS-}b\text{-VAc}$$

The general procedure for block copolymerization of vinyl acetate and styrene is as follows. Vinyl acetate was polymerized in Terrasail for 4 h at 70 °C using BPO as initiator. Then a predetermined amount of styrene was introduced via vacuum distillation followed by heat-sealing the reactor from the vacuum line. The reaction was allowed to

proceed for 4 days at room temperature. To stop the reaction, the mixture was precipitated in ethyl ether. The crude polymer was dissolved in THF, re-precipitated in ethyl ether three times, and then was dried for further characterization. Methanol and cyclohexane were used to Soxhlet-extract any homopolymers of poly(vinyl acetate) and polystyrene, respectively.

A control experiment has been carried out to see if Soxhlet-extraction is an effective way to purify our polymers: Equal amount of PS and PVAc homopolymers (mol_{PVAc}: mol_{PS} = 1:1) were Soxhlet-extracted using methanol for 3 days, than the sample was dried and its ^1H NMR showed that only PS homopolymer existed. After another 3 days of Soxhlet-extraction using cyclohexane, no solid samples were left.

VAc monomers are preferentially polymerized first due to several factors. First, VAc is easily dissolved in Terrasail while PVAc precipitates from the reaction medium. Secondly, styrene, which is soluble in Terrasail, copolymerizes much faster than VAc as discussed above, thus St monomer aggressively reacts with PVAc chains more preferentially than VAc monomers due to the large difference in reactivity ratios. This advantage also allowed direct addition of styrene monomers without pumping away unreacted vinyl acetate monomers. Characteristics of the resulting polymers are summarized in **Table B-3.**

A great increase of incorporated vinyl acetate units (from 9% to 50%) could be attributed to the increased ratio of first monomer (vinyl acetate) to initiator (from 1ml/20mg to 1.5ml/20mg). The higher the molecular weight of poly(vinyl acetate), the longer the polymer chain, and thus in this study, the better the “living” radical chain ends are preserved. The decreased overall molecular weight and yield may due to the larger

Table B-3 Preparation of PVAc-b-PS using BPO at 70°C in Terrasail

Run	PVAc block		Block copolymers			Yield (%)[d]
	M_n (*10^{-5})	PDI	M_n (*10^{-5})	PDI	Composition (VAc mol%)[c]	
V3S2[a]	0.67	1.22	6.00	3.41	50.00	2.27
V2S2[b]	0.37	1.90	10.81	2.14	9.09	8.12

[a]VAc/St/IL/BPO=3ml/2ml/5ml/40mg.

[a]VAc/St/IL/BPO=2ml/2ml/5ml/40mg.

[c]Obtained from ^{1}HNMR.

[d]Calculated gravimetrically.

amount of residue vinyl acetate monomers after polymerization of the first block. In sample V3S2 (VAc/St=3ml/2ml), the unreacted vinyl acetate monomers acted as diluent during the addition of the second monomer (St), and thus facilitated the termination reaction of polymer chains.

Figure A-6 shows the SEC (size exclusion chromatography) trace of sample V2S2 (VAc/St=2ml/2ml). Unavoidably there is PVAc homopolymer present in the un-extracted block copolymers. The actual amount of PVAc homopolymer by mass is underestimated in **Figure A-6** because the dn/dc value for PVAc in THF (dn/dc = 0.052 ml/g) is lower than that for PS (dn/dc = 0.189 ml/g). However, after extraction by methanol (solvent for PVAc and nonsolvent for PS), the peak representing PVAc homopolymer disappeared. The existence of PS homopolymer was observed after extraction using cyclohexane (solvent for PS above room temperature and nonsolvent for PVAc). Since the addition and polymerization of the second monomer (St) was carried out at room temperature, the

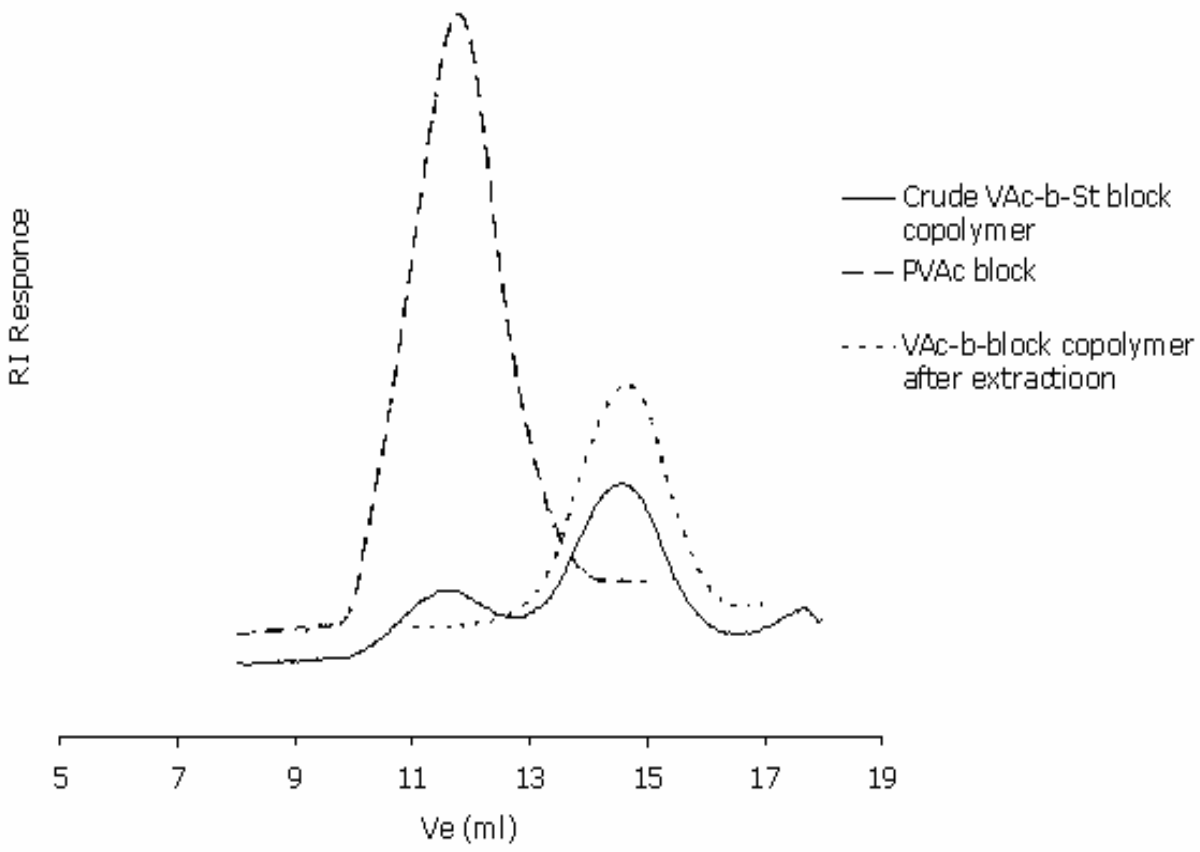


Figure A-6. SEC traces of St-VAc block copolymers (V2S2 in **Table B-3**)

half-life of BPO ($t_{1/2}$) at 25 °C is more than 45,000 h as calculated from the Arrhenius equation (K_d=A*exp$^{-Ea/RT}$) and the initiation rate equation ($t_{1/2}$ = ln 2/K_d), with E_a = 139.0 kJ mol^{-1}, R = 8.314 J mol^{-1}K^{-1}, and A = 9.34*10^{15} s^{-1}, the production of PS homopolymer was unlikely to be caused by the initiation of BPO, but the chain transfer of PVAc radicals to St monomer as vinyl acetate propagating radicals have very high reactivity. The final products were further characterized by DSC and IR.

Figure A-7 and **Figure A-8** show the DSC traces of sample V2S2 (VAc/St=2ml/2ml) and V3S2 (VAc/St=3ml/2ml), respectively. Two distinct glass transition temperatures (T_g) corresponding to PS and PVAc blocks can be clearly seen in **Figure A-8**, reflecting the formation of two immiscible phases from PS and PVAc blocks (St mol%: VAc mol% = 1:1). The composition was calculated from ^{1}H NMR spectra as shown in **Figure A-10**. However, only a single intermediate T_g (95.29°C) close to that of PS homopolymer (T_g=100°C) is observed in **Figure A-7**. This homogeneity was caused by inability of a small amount of PVAc (<10 mol%) units to induce the phase separation. The distinct small peak around 5 ppm in the ^{1}H NMR spectra, as shown in **Figure A-9**, clearly demonstrates that the polymers do contain vinyl acetate units. IR spectra of sample V3S2 (VAc/St=3ml/2ml), as shown in **Figure A-11**, also verify the presence of both styrene units and vinyl acetate units. Peaks around 3028 cm^{-1} are due to the C-H stretching of the benzyl ring of styrene units. The peak at 1737 cm^{-1} depicts the C=O stretch of vinyl acetate units.

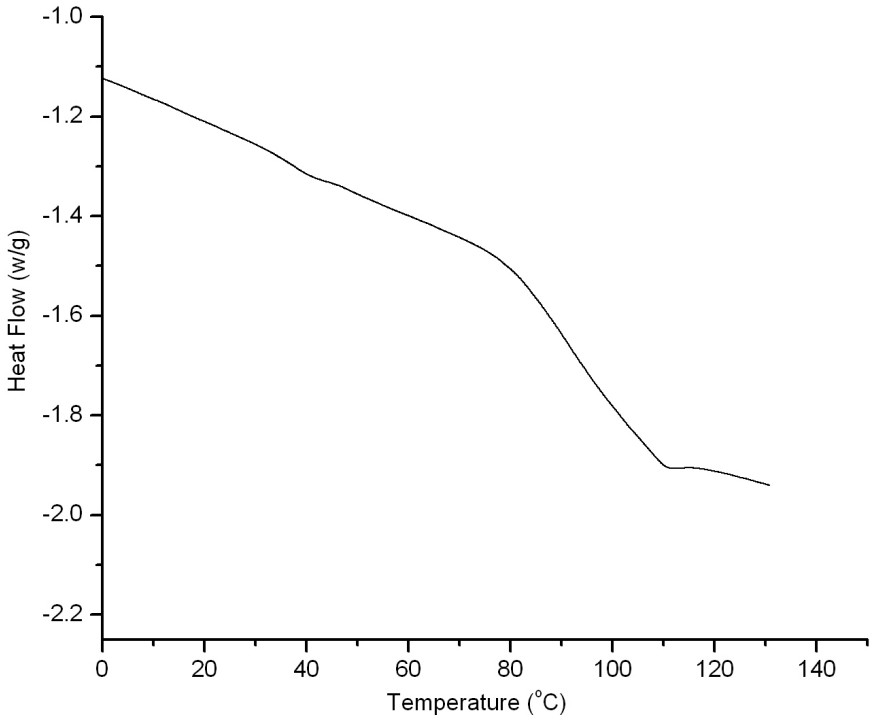


Figure A-7. DSC trace of sample V2S2 (VAc/St=2ml/2ml)

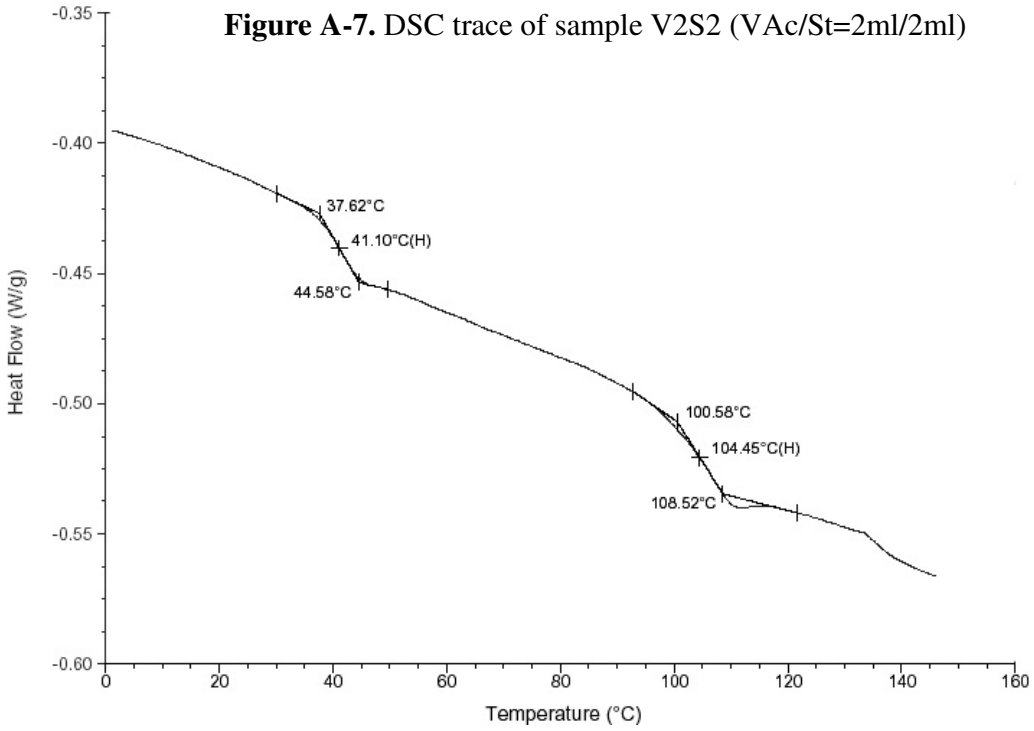


Figure A-8. DSC trace of sample V3S2 (VAc/St=3ml/2ml)

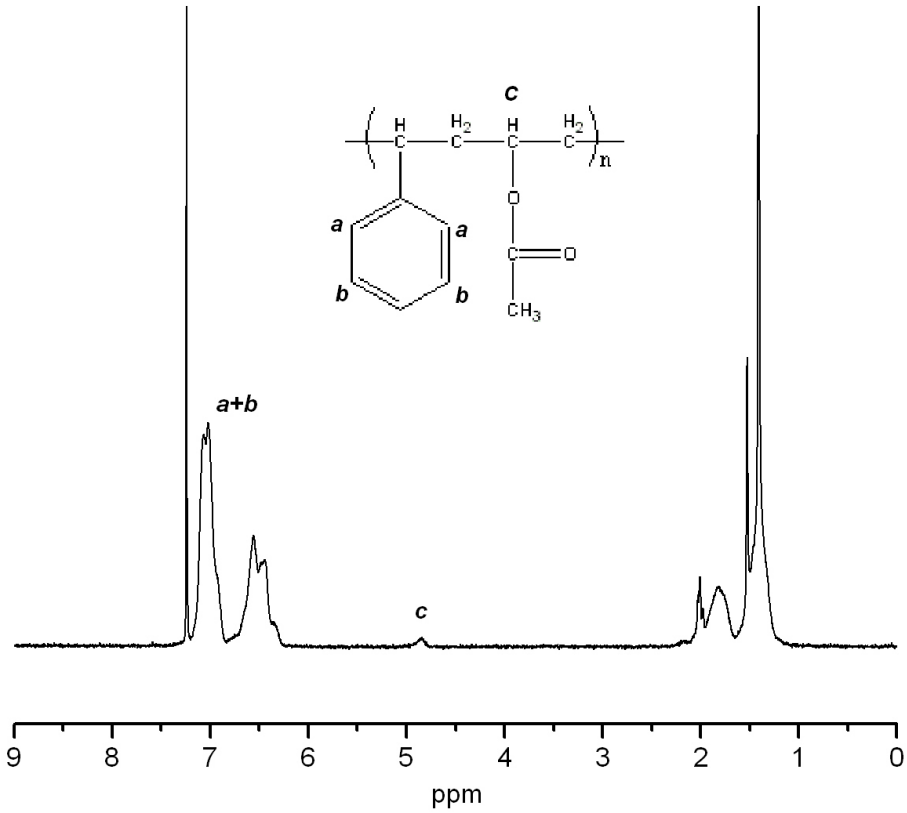


Figure A-9. ^{1}H NMR spectra of sample V2S2 (VAc/St=2ml/2ml)

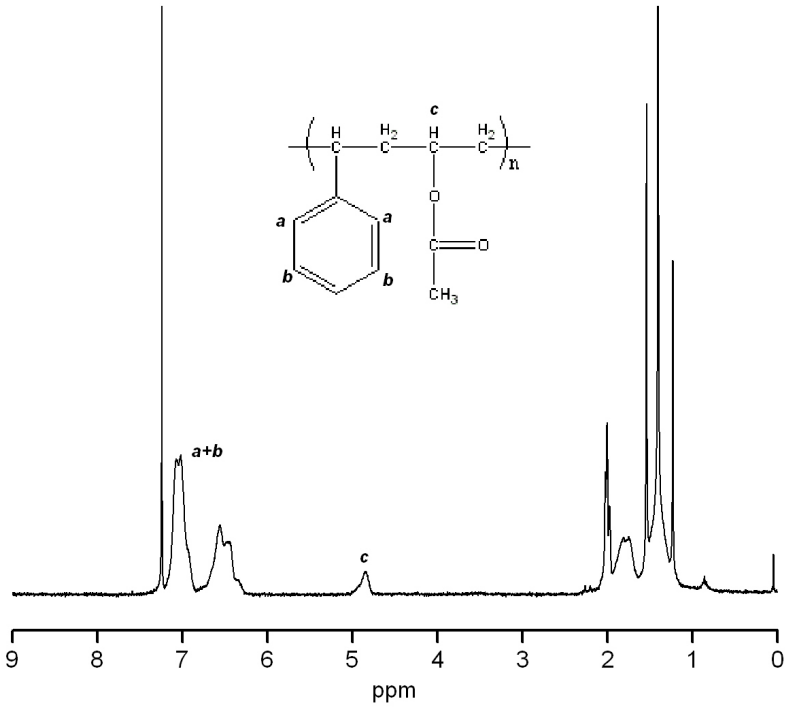


Figure A-10. ^{1}H NMR spectra of sample V3S2 (VAc/St=3ml/2ml)

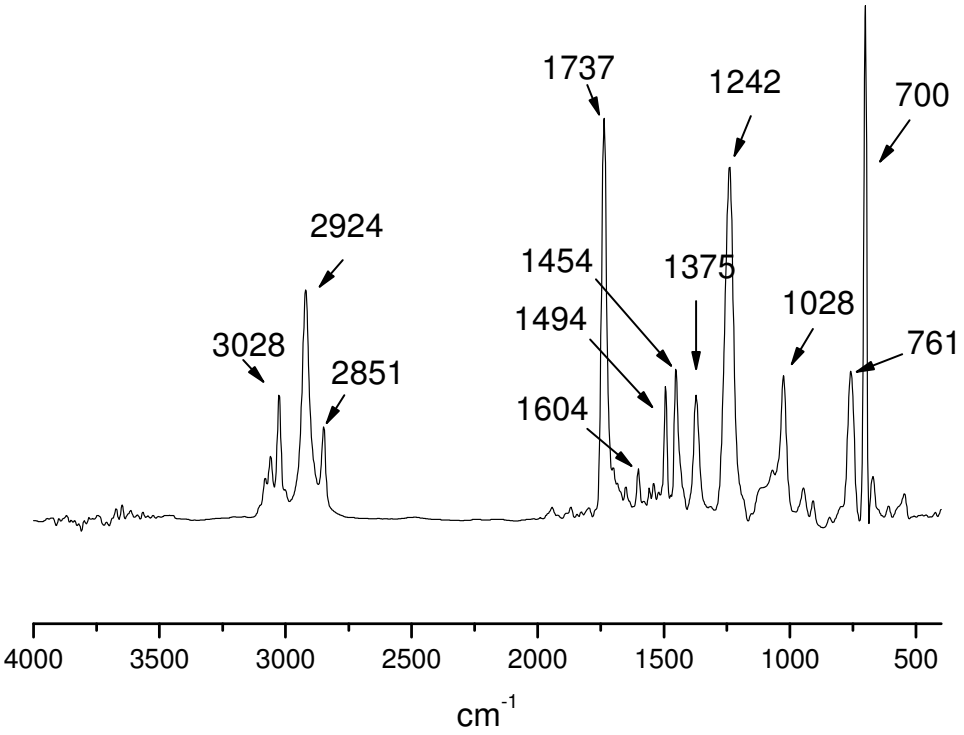


Figure A-11. IR spectra of V3S2 (VAc/St=3ml/2ml)

3.2.2 Sequential Block Copolymerization of Styrene and Acrylic Acid

3.2.2.1 Sequential Polymerization of Styrene and tert-Butyl Acrylate (t-BA)

Our first attempt involved tert-butyl acrylate (t-BA) as a protected precursor to PAA.

The general procedure was carried out as below: polymerizing the first block (styrene) for a short time (4 hours) at elevated temperatures (70 °C), followed by removal of residual monomer under vacuum, followed by introducing of the second monomer (t-BA), and allowing the reaction to proceed at room temperature for 3-4 days.

The crude copolymers were Soxhlet-extracted with methanol to remove the homo-PtBA contaminant formed during the second block formation. Methanol is a marginal solvent for PtBA. A blank experiment was first tried to see whether or not methanol could dissolve high molecular weight PtBA synthesized by bulk polymerization under Soxhlet extraction. The results were positive and high molecular weight PtBA was completely removed by extraction for three days. After hydrolysis and dialysis to hydrolyze the ester group and remove any impurities during the hydrolysis process, the PtBA was converted to PAA (poly(acrylic acid)). Then samples then were Soxhlet-extracted using cyclohexane to remove any PS homopolymers. After extraction, the samples were dried for further characterization.

However, ^{1}H NMR spectra indicated that only pure polystyrene homopolymers formed, as shown in **Figure A-12**. The failure to obtain the targeted block copolymers may be attributed to the fact that the second monomer, tert-butyl acrylate, is partially soluble in [BMIM]PF_6. Since propagation of the second block is diffusion-controlled, poor solubility prohibits tert-butyl acrylate from reaching PS chain ends.

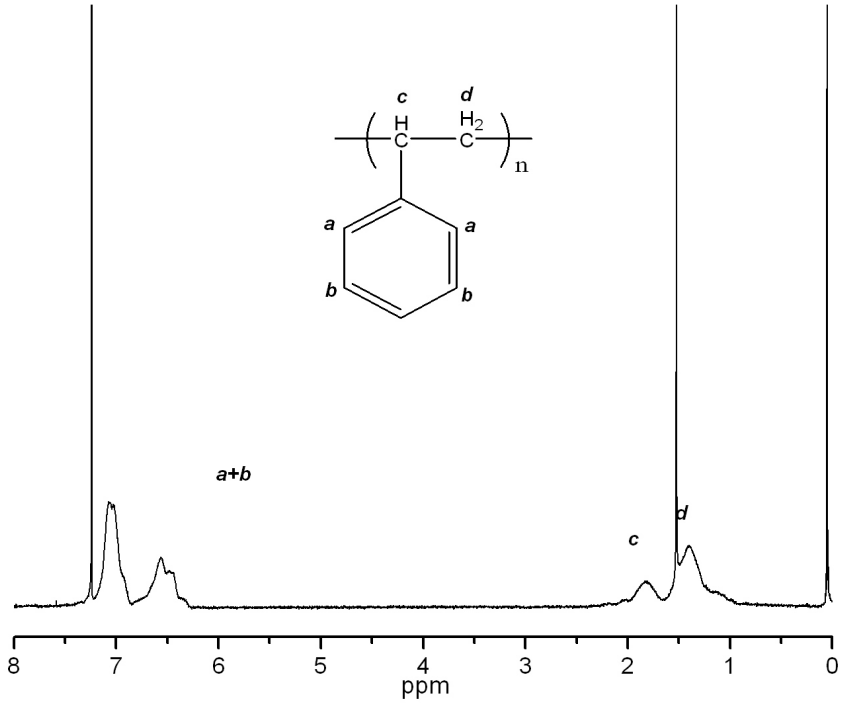


Figure A-12. ^{1}H NMR spectra of the final product of sequential block copolymerization of St and t-BA

3.2.2.2 Sequential Block Copolymerization of Styrene and Acrylic Acid

Solubility test shows that acrylic acid is miscible with the ionic liquid [BMIM]PF_6 and PS homopolymers are insoluble in this ionic liquid, thus there is a possibility that blocky copolymers could be formed if polymerizing these two monomers in a sequential manner with styrene being the first monomer.

The general procedure followed is as described before. Acetone was used to extract products out of RTILs. Methanol and cyclohexane were used to Soxhlet-extract any homopolymers of poly(acrylic acid) and polystyrene, respectively. ^{1}H NMR was then employed to characterize the obtained polymers.

Figure A-13A shows ^{1}H NMR spectra of the final product; **Figure A-13B** shows ^{1}H NMR spectra of PAA homopolymer. The typical peak around 2.2 ppm^{-1} representing α-H of PAA backbone (shown as 'a' in **Figure A-13B**) cannot be clearly seen in **Figure A-13A**. Both of the two spectra demonstrated a sharp singlet around 3.5 ppm, which was attributed to the mobile proton on the carboxyl group. Thus, it could be concluded that in the sequential polymerization of styrene and acrylic acid, only a few units of acrylic acid grew into the PS radical chains. This may partly because acrylic acid is so reactive, that during the diffusion process it self-polymerizes.

3.3 Conventional Free Radical Homopolymerization of HEMA in Room Temperature Ionic Liquids

It is agreed that RTILs are able to increase rate constant of the propagation while decrease that of termination for the free radical polymerization of alkyl methacrylates. Therefore, both higher overall polymerization rate and higher molecular weight were observed.[38-43]

Herein we studied free radical polymerization of HEMA in three different types of room temperature ionic liquids (Structures of them are shown in **Figure A-1; Figure A-2; Figure A-3; Figure A-4**). Our results showed that the positive effects of employing ionic liquids as the reaction medium extended from polymerization of alkyl methacrylate (methyl methacrylate) to that of functional methacrylates (HEMA).

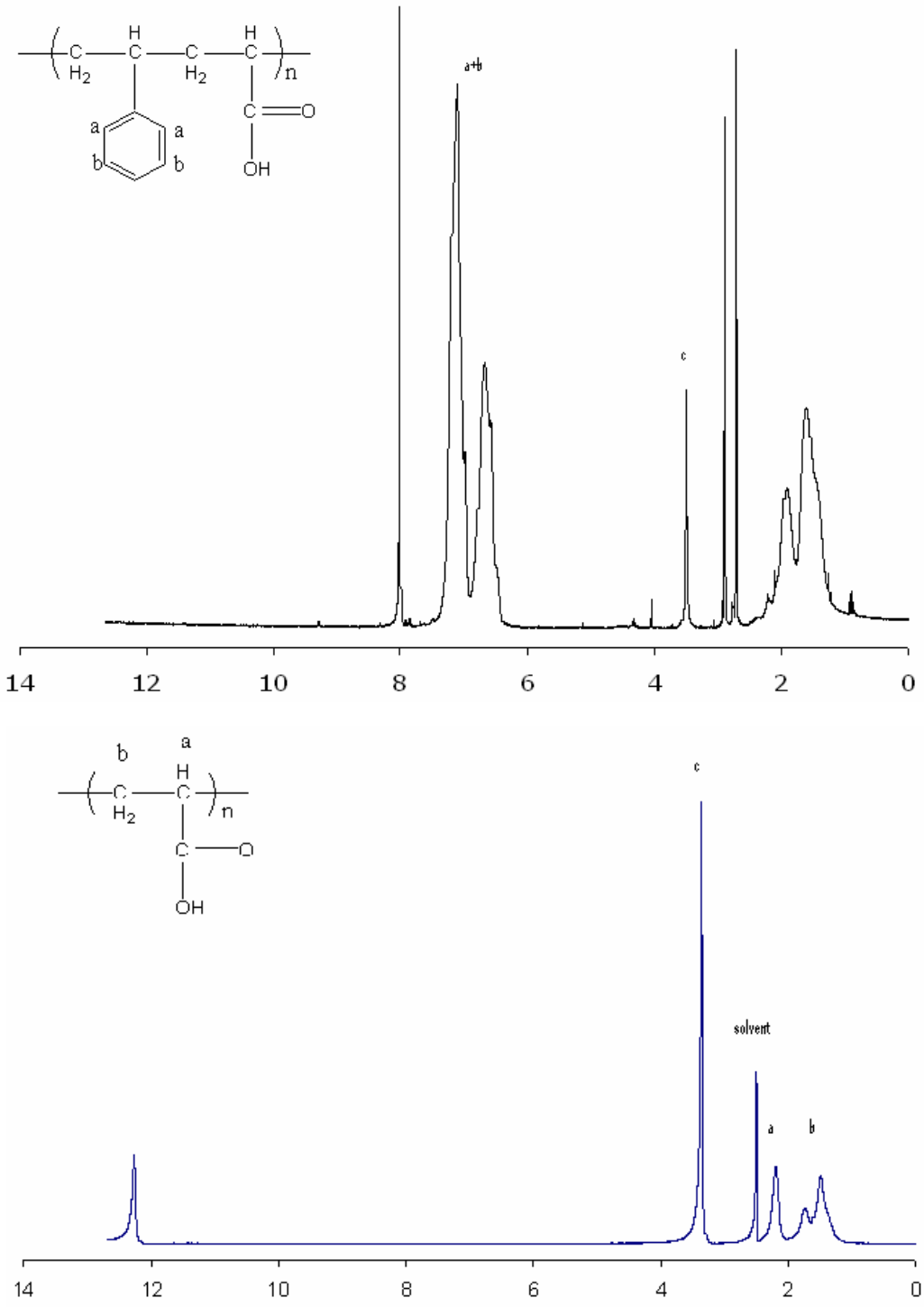


Figure A-13 ^{1}H NMR Spectra of A) the final product of sequential block copolymerization of St and AA; B) PAA homopolymer

All polymerizations were performed under a dry nitrogen atmosphere. The initiator, monomers and reaction media were weighed and measured into flasks separately. After bubbling with dry nitrogen for 30 minutes, the flasks were kept in a water bath at 70°C for the desired time. The polymerizations were stopped by precipitation into appropriate organic solvents. After the decanting of solvent, the crude polymer was dissolved in THF and re-precipitated repeatedly, then dried under vacuum to constant weight. Conversions were determined gravimetrically.

To extract resulting polymers out of RTILs, appropriate organic solvents (ethyl acetate for [BMIM]PF_6, and water for Marisail) were chosen. When methanol was used as polymerization medium, the reaction mixture was allowed to sit at room temperature to evaporate the solvent, and then dried to obtain pure polymer. Results are summarized in **Table B-4.**

HEMA polymerized very fast in the three RTILs employed, and in general, the resulting products possessed higher molecular weights than those polymers obtained in methanol. When monomer concentrations were relatively high (1:5), gelation occurred for all three polymerizations in RTILs within less than an hour. Especially in Terrasail, the most viscous RTILs of the three, the system still gelled even if monomer concentration was lowered to 1:10, and polymer was very difficult to isolate from the gel.

[BMIM]PF_6 was the best of the three RTILs in terms of obtaining high molecular weight polymers. The SEC trace of poly(HEMA) obtained from [BMIM]PF_6 (HEMA : [BMIM]PF_6 = 1:10 (v/v)) displayed two apparent peaks as shown in **Figure A-14**, which, however, could be the splits of one peak, due to the ultra high molecular weight, which is out of the instrument's operating range. The unexpectedly high molecular weight of this

Table B-4 Homopolymerization of HEMA (2-hydroxyethyl methacrylate) in three different room temperature ionic liquids

	HEMA : Solvent = 1:5 (v/v)				HEMA : Solvent = 1:10 (v/v)			
	Run	Time (hr)	Yield (%)[b]	M_n*10^{-5} (M_w/M_n)	Run	Time (hr)	Yield (%)[b]	M_n*10^{-5} (M_w/M_n)
Terrasail	1	0.3			5	1.5		
$[BMIM]PF_6$	2	0.5	73	8.45 1.44	6	4	76	24.27 1.10 3.38
Marisail	3	0.8	42	9.44 1.75	7	4	36	1.82 10.65 1.66
Methanol	4	4	52	2.41 1.57	8	4	40	2.73 1.29

[a]HEMA/BPO=1ml/20mg.

[b]Calculated gravimetrically.

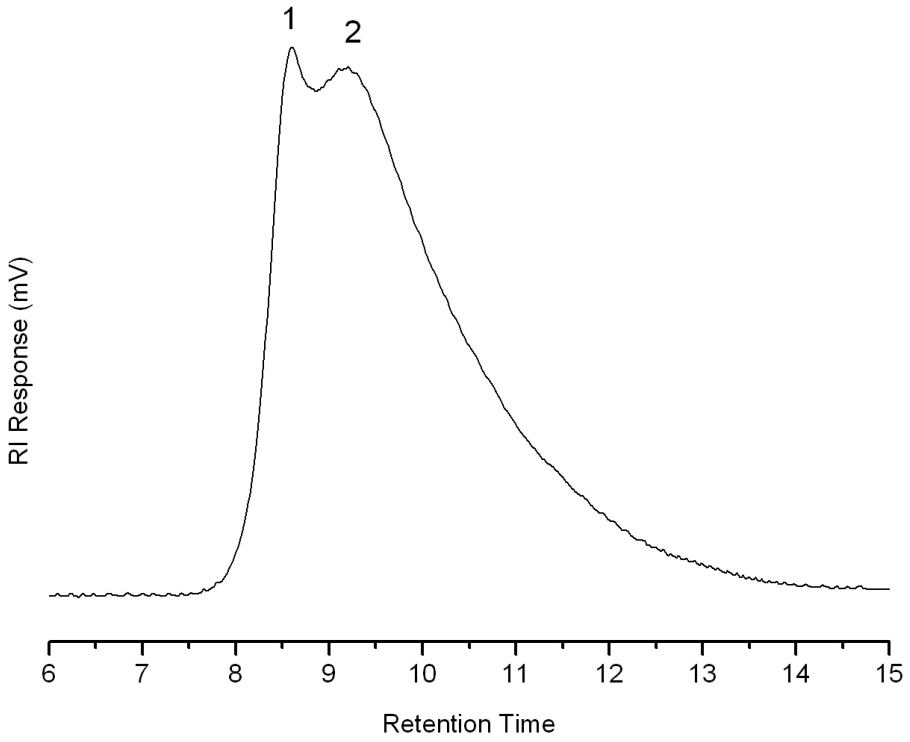


Figure A-14. Sec trace of poly(HEMA) obtained from [BMIM]PF_6 (HEMA : [BMIM]PF_6 = 1:10 (v/v), as Run 6)

poly(HEMA) may be attributed to [BMIM]PF_6's mildly high viscosity as well as its partial miscibility with generated poly(HEMA). Therefore, [BMIM]PF_6 could be a potential polymerization medium for the synthesis of ultra high molecular weight poly(HEMA).

However, in regard to "green chemistry", Marisail was the most ideal of the three RTILs, due to the fact that 1) no volatile organic solvent was used during the whole process; 2) polymer can be easily recovered simply by precipitation from water. Furthermore, the molecular weight of the obtained poly(HEMA) reached as high as 10^6, which was 4 times higher than that obtained from polymerization in methanol under identical polymerization conditions.

Strehmel *et al*.[49] found that the higher viscosity, the higher yields and molecular weights of the polymers. Zhang *et al*.[44], however, stated that their attempts to correlate viscosity with polymerization behavior failed. This discrepancy could be attributed to two different procedures the two groups followed. Strehmel *et al.* carried out the polymerizations to relatively high conversions, while Zhang *et al.* tended to keep conversions low to avoid so called "Trommsdorff effect". We also carried out viscosity tests of the three RTILs, and results are summarized in **Table B-5.** However, our study failed to show any clear correlations between the viscosities of the RTILs and the polymerization behavior under the conditions we employed.

Table B-5 Correlations between viscosities of RTILs and the characterization data for poly(HEMA) produced in RTILs

Ionic Liquids	Viscosity (cp)	HEMA : Solvent = 1:5 (v/v)			HEMA : Solvent = 1:10 (v/v)		
		Time (hr)	Yield (%)[b]	M_n*10^{-5} (M_w/M_n)	Time (hr)	Yield (%)[b]	M_n*10^{-5} (M_w/M_n)
Terrasail	518.07	0.3			1.5		
$[BMIM]PF_6$	48.65	0.5	73	8.45 1.44	4	76	24.27 1.10 3.38
Marisail	33.05	0.8	42	9.44 1.75	4	36	1.82 10.65 1.66

[a]HEMA/BPO=1ml/20mg.

[b]Calculated gravimetrically.

Another interesting trend witnessed is that, for RTILs, as the systems was diluted (volume fraction of monomer was lowered from 1/6 to 1/11), molecular weights were higher, which is usually not the case in conventional organic solvents. This may be attributed to the RTILs' ability to preserve "living" polymer chain radicals, which is at least partly caused by higher viscosities of ionic liquids. Hong *et al.*[40] described it as a "diffusion-controlled termination" mechanism to explain this diminished chain terminations in viscous systems. Thus, the more diluted the system was, the less chance for two polymer chain radicals to react with each other, the more time for monomers to react with the chain ends.

3.4 Copolymerization in Room Temperature Ionic Liquids

The motivation for us to try free radical copolymerization in RTILs is the assumption that the RTILs are able to keep polymer macroradicals "living". Furthermore, if there is a big difference between the reactivity ratios of the two monomers, which is, one monomer polymerizes much faster than the other one when co-existing in the polymerization system, then there is a chance to obtain blocky copolymer. Three different polymerization systems were chosen to test out this method: St/VAc/Terrasail (r_{st}= 18.8; r_{VAc}= 0.02[89]), St/AA/[BMIM]PF_6 (r_{st}=0.253; r_{aa}=0.136) and St/HEMA/Marisail (r_{st}=0.5, r_{HEMA}=1.65 [90]).

3.4.1 Copolymerization of Styrene with Vinyl Acetate in Terrasail

3.4.1.1 Homopolymerization of Styrene and Vinyl Acetate

The procedure has been described in the experimental section. Generally, the polymerizations were carried out in Terrasail for 4 h at 70 °C using benzoyl peroxide as initiator under a nitrogen atmosphere. Then the reaction mixture was poured into methanol for styrene (St) or ethyl acetate for vinyl acetate (VAc). After the decantation of solvent, the crude polymer was dissolved in tetrahydrofuran (THF) and reprecipitated in methanol or ethyl acetate repeatedly, then dried under vacuum to obtain pure PS. Results are listed in **Table B-6.**

It is interesting that the rates of polymerization (reflected in yields) initially increase on dilution with Terrasail to rates faster than for bulk polymerization, and only decrease slightly with further dilution. Molecular weights and PDIs are not strongly affected by the level of RTIL addition (normally dilution decreases M_n in free radical polymerization). In contrast to the behavior of styrene, with VAc the conversion, molecular weight, and PDI all decreased with the increase of ratio of ionic liquid to monomer.

3.4.1.2 Copolymerization of Styrene and Vinyl Acetate

Copolymerizations of styrene and vinyl acetate were carried out under nitrogen atmosphere in Terrasail as solvents. Distilled monomers, initiators (BPO) and Terrasail were added together. Reactions were stopped by quenching the mixtures into ethyl ether. Results are listed in **Table B-7.**

Table B-6 Effect of Terrasail on the homopolymerization of styrene (St) and vinyl Acetate (VAc)

Monomer / [M] : [IL] [a]	M=St			M=VAc		
	Yield (wt%)[b]	M_n(*10^{-4})	PDI	Yield (wt%)[b]	M_n(*10^{-4})	PDI
1:1	23	4.1	1.91	40	5.9	2.58
1:2	28	4.3	1.88	35	4.5	1.84
1:3	36	3.7	1.93	37	4.3	1.88
1:4	34	4.6	2.24	25	3.2	1.79
1:5	32	4.0	2.20	10	2.9	1.58

[a]Monomer /BPO=1ml/20mg.

[b]Calculated gravimetrically.

Table B-7 Characteristics of random copolymerization of styrene (St) and vinyl acetate (VAc)

Run	Solvent (Terrasail) (ml)	Monomers (ml)	Initiator (BPO) (mg)	Reaction Temp. (°C)	Time (hr)	Yield (%)[a]	$M_n(*10^{-4})$ (M_w/M_n)
1	25 (ml)	St (10ml) VAc (10ml)	400	70	4	24.20	1.5 1.70
2	25 (ml)	St (10ml) VAc (10ml)	400	70	19	54.09	1.2 1.88
3	25 (ml)	St (5ml) VAc (10ml)	100	75	15		3.5 1.66

[a]**Calculated gravimetrically.**

^{1}H NMR was used to characterize the obtained polymers, and showed that only polystyrene homopolymers were formed, as shown in **Figure A-15**. It was noticed that few vinyl acetate units were incorporated in the obtained polymers, even with an increase of the reaction time (Run 2, from 4 hours to 19 hours; Run 3, from 4 hours to 15 hours), or with the increase of reaction temperature (Run 3, from 70°C to 75°C). The formation of PS homopolymerization is not surprising since during copolymerization with VAc, St tends to polymerize much faster than VAc, as indicated by the big differences of their reactivity ratios (r_{st} is over 900 times higher than r_{VAc}). Furthermore, our results suggest that even in the case of long-lived PS radicals there is little tendency for VAc to react, even at long times when styrene is nearly consumed.

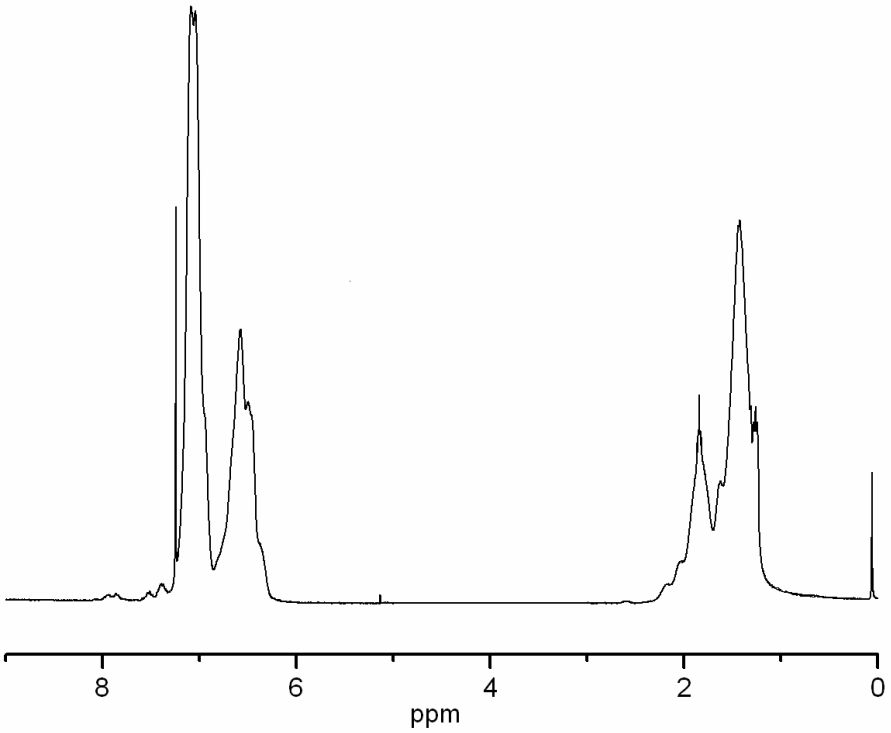


Figure A-15. ^{1}H NMR spectra of obtained polymer from random copolymerization of St with VAc (Run 2)

3.4.2 Copolymerization of Styrene and Acrylic Acid

Polymerization was carried out using the general procedure as described in the Experimental section. To stop the reaction, the solution was poured into acetone. A rough test for block copolymer formation was done by dissolving a few samples in 1/1 (v/v) THF-water mixture, resulting a clear solution. Adding several drops of either THF or water gives a cloudy light blue color, which shows possible formation of micelles. ^{1}H NMR and DSC were then employed to further characterize the obtained polymer. However, ^{1}H NMR spectra, as shown in **Figure A-16**, clearly demonstrate that the polymers are of a random nature since a cluster of peaks which are assigned to the benzyl group of styrene units would indicate that not every styrene unit is next to each other, thus most probably that a random order of styrene-acrylic acid copolymer is formed instead of the blocky copolymer. For DSC result, since two T_gs of the components are so close to each other (T_g = 106 ^{o}C for PAA; T_g = 100 ^{o}C for PS), methylation of PAA units was conducted in order to distinguish PAA units from PS units via their T_gs. (Procedure of methylation was: 50 mg sample was dissolved in a mixture of THF and water (overall volume = 10ml). The yellow solution of trimethylsilydiazomethan was added dropwise at room temperature into the copolymer solution. Upon addition, bubbles appeared and the solution became slowly colorless. Addition of the methylation agent was continued until the solution remained yellow and stopped bubbling.) However, no clear evidence of the formation of blocky copolymer was observed as only one unexpected low glass transition temperature was observed by DSC, as shown in **Figure A-17**. The low T_g (4.5 ^{o}C), which is lower than that of either homopolymer ($T_{g\mathrm{PMA}}$ = 10 ^{o}C, $T_{g\mathrm{St}}$ = 100 ^{o}C), may due to the presence of residual RTIL.

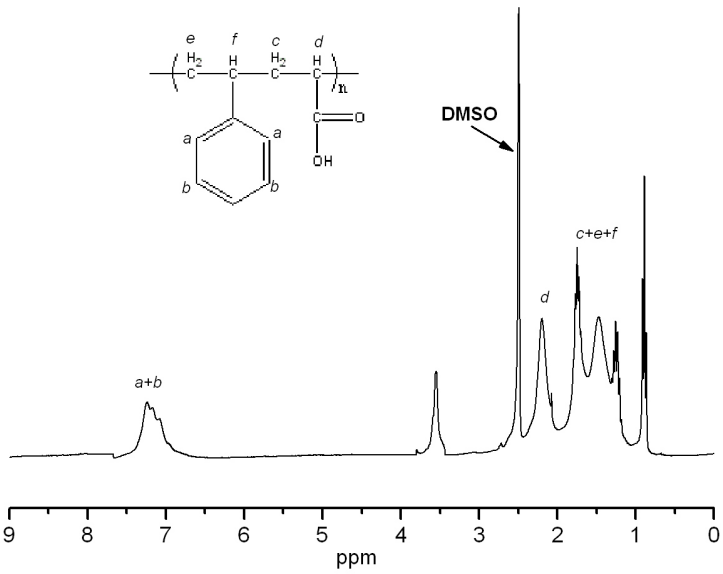


Figure A-16 ^{1}H NMR spectra of obtained polymer from copolymerization of St with AA

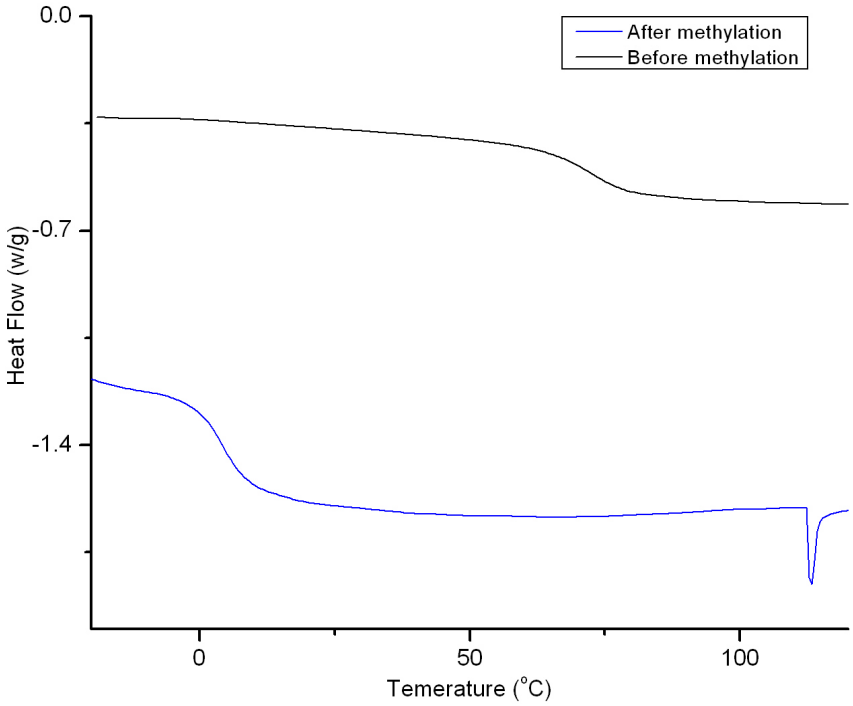


Figure A-17. DSC Traces of obtained polymer from copolymerization of St with AA

3.4.3 Copolymerization of HEMA with Styrene

Our previous experience in homopolymerization of HEMA showed that HEMA polymerizes very fast in RTILs, allowing more time for styrene to attach to the radical chain ends. For "green chemistry" considerations, Marisail was studied as a reaction medium.

Polymerization was carried out by injecting equal volumes of the two monomers at the same time under a dry nitrogen atmosphere, followed by bubbling the whole system with nitrogen for 30 min. Then the polymerization was allowed to proceed at 70^{o}C for 4 h. Distilled water was used to extract polymers out of RTILs. Characteristics of the resulting polymers are listed in **Table B-8.**

From ^{1}H NMR spectra, as shown in **Figure A-18**, the peaks between 0 ppm and 2 ppm could be attributed to the resonances of a styrene unit next to a HEMA unit, which clearly demonstrated that random copolymers formed. Furthermore, DSC data, as shown in **Figure A-19,** give a single T_g of 96.08 ^{o}C, which agrees well with the one (93.43 ^{o}C) calculated from ^{1}HNMR and the equation $1/T_g = (w_1/T_{g1}) + (w_2/T_{g2})$. ($T_g$-apparent glass transition temperature of the two component system; w_1, w_2-weight percentage of the two components respectively; T_{g1}, T_{g2} –glass transition temperature of the two components respectively.)

Table B-8 Characteristics of Copolymers of HEMA with St

Solvent	Monomers	Reactivity Ratios	Yield (%)[b]	M_n (* 10^{-5})	PDI	Composition (wt%)
Marisail (25ml)	St (5ml), HEMA (5ml)	r_{st}= 0.5; r_{HEMA}= 1.65	33.72	7.95	2.23	42.8 (HEMA%)

[a]Monomer Pair/BPO=(5+5)ml/100mg.

[b]Calculated gravimetrically.

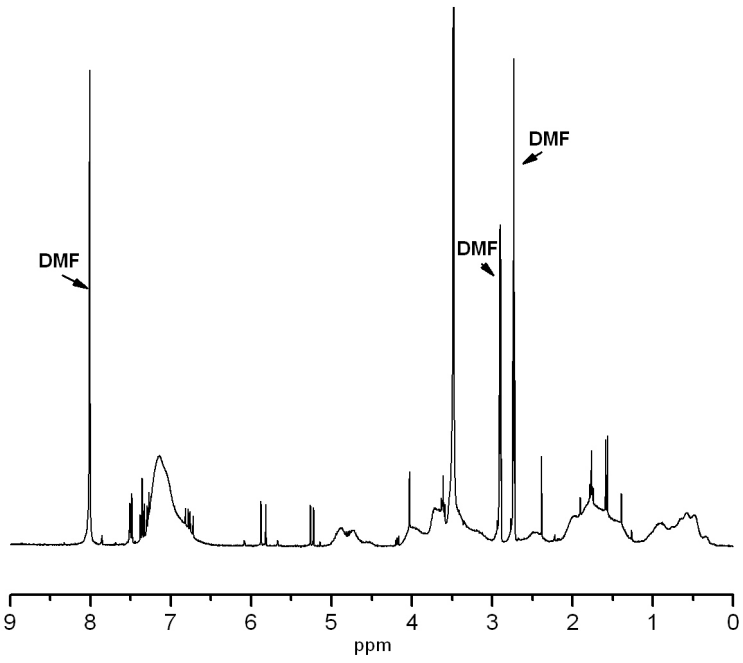


Figure A-18. ^{1}H NMR Spectra of obtained polymer from copolymerization of St with HEMA

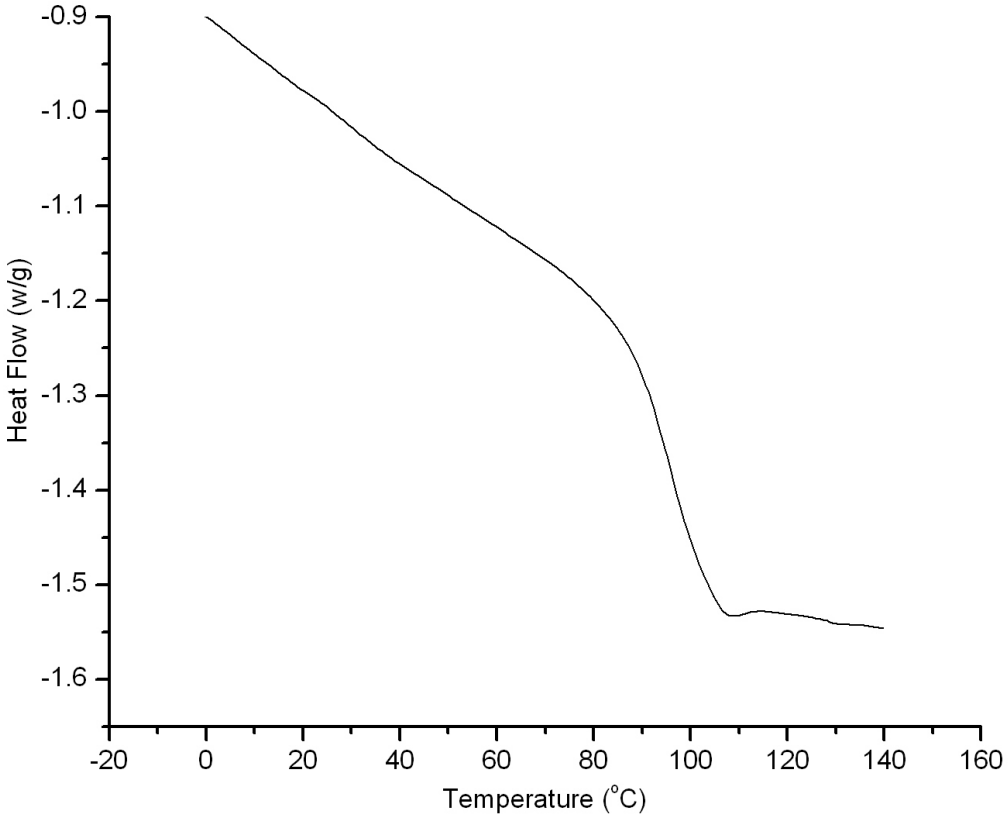


Figure A-19. DSC Trace of obtained polymer from copolymerization of St with HEMA

4 Conclusions

Sequential addition free radical polymerization in RTILs was applied to three polymerization systems: the St/VAc monomer pair in Terrasail, the St/tBA monomer pair in [BMIM]PF_6 and the St/AA monomer pair in [BMIM]PF_6. The monomers pairs were selected according to the solubility tests in the four RTILs based on the following considerations: 1) the macro radicals obtained from the first monomer should be immiscible with the RTIL; 2) the second monomer should be soluble in the RTILs. The synthesis of styrene vinyl acetate block copolymer was made via two routes: styrene as the first monomer, vinyl acetate as the second; and the reverse order. While the first route only yielded polystyrene homopolymers, block copolymers of St and VAc were obtained via the second route. The molecular weight of the product was as high as $6 * 10^5$ with a composition of 50% (VAc mol%). However, the overall yield was low (2.27%), as a result of chain transfer reactions of vinyl acetate macro radicals. For the pair of styrene and tert-butyl acrylate, the reaction medium was [BMIM]PF_6. However, only pure polystyrene homopolymers were obtained. When acrylic acid was used as the second monomer, the final product was mainly polystyrene with a few acrylic acid units incorporated. The unstable results indicated that sequential addition free radical polymerization in RTILs is not effective on all polymerization systems. The choice of appropriate RTILs may be a critical factor in order for this strategy to be successful. Furthermore, we used BPO as the initiator for all our polymerizations. However, since the residual BPO cannot be pumped away by vacuum, the polymerization of the second monomer needs to be done under room temperature in order to avoid the decomposition

of the residual BPO. This might be solved by using volatile thermoinitiators rather than BPO, or by switching to photoinitiation.

Free radical copolymerization of St with VAc, St with AA and St with HEMA were also carried out in RTILs. Far from our expectations, both St/VAc and St/HEMA monomer pairs yielded random copolymers, while only PS homopolymer was obtained for the pair of St/VAc. The generation of pure PS homopolymer, however, is not surprising since during copolymerization with VAc, St tends to polymerize much faster than VAc, based on their reactivity ratios (r_{st} is over 900 times higher than r_{VAc}). Our results further suggest that even in the case of long-lived PS radicals there is little tendency for VAc to react, even at long times when styrene is nearly consumed. These results failed to show any dramatic effects of RTILs on the free radical copolymerization, although RTILs are believed to be able to enhance the rates of propagation while depressing the rates of termination in homopolymerizations.

Free radical homopolymerization of HEMA was carried out in four different RTILs. All of the reactions exhibited very high polymerization rates, and the resulting products exhibited higher molecular weight than those polymers obtained in methanol. Therefore, the positive effect of employing RTILs as polymerization medium has been extended from alkyl methacrylates to functional methacrylates. RTILs are a potential reaction medium for producing ultra high molecular weight poly(HEMA).

Additionally, homopolymerization of styrene and vinyl acetate was carried out in Terrasail via conventional free radical polymerization. We observed that the two monomers exhibit different behaviors. For the polymerizations of vinyl acetate, with an increase of the ratio of ionic liquid to monomer, the conversion, molecular weight and

PDI all decreased. However, for the polymerizations of styrene, the rates of polymerization initially increase on dilution with Terrasail and only decrease slightly with further dilution. The molecular weights and PDIs are not strongly affected by the level of RTIL addition.

List of References

1. *Walden, P., Acad. Imper. Sci. (St. Petersburg), 1914: p. 1800.*
2. *Hussey, C.L., Pure Appl. Chem. , 1988.* ***60****: p. 1763-1772.*
3. *Seddon, K.R., Mamantov, G., Eds., . 1987, Dordrecht, The Neverlands: Reidel Publishing Co. 365.*
4. *Wilkes, J.S.L., J. A.; Wilson, R. A.; Hussey, C. L. , Inorg. Chem. , 1982.* ***21****: p. 1263-1264.*
5. *Hussey, C.L., Advances in Molten Salts Chemistry, ed. G.M. Mamantov, C. Vol. 5. 1983, New York. 185-230.*
6. *Dieter, M.K.D., C. J. Jr.; heimer, N. E.; Rovang, J. W.; Wilkes, J. S., J. A. Chem. Soc., 1988.* ***110****: p. 2722.*
7. *Ngo, H.L.L., K.; Hargens, L.; McEwen, A. B., Thermochim. Acta, 2000.* ***357-358****: p. 97-102.*
8. *Wilkes, J.S.Z., M. J., J. Chem. Soc., Chem. Chem. Commun., 1992: p. 965.*
9. *Earle, M.J., Esperança, J.M.S.S.; Gilea,M. A.; Lopes, J.N.C.; Rebelo, L.P.N.; Magee, J.W.; Seddon, K.R. and Widegren, J.A., Nature, 2006.* ***439****: p. 831.*
10. *Cornils, B.H., W. A., Applied Homogeneous Catalysis with Organometallic Compounds, B.H. Cornils, W. A., Editor. 1996: Weinheim, New York. p. 1167.*
11. *Chauvin, Y.M., L.; Olivier, H., Angew. Chem. Int. Ed., 1995.* ***34****: p. 2698.*
12. *Dullius, J.E.L.S., P. A. Z.; Einloft, S.; de Souza, R. F.; Dupont, J.; Fischer, J.; De Cian, A., Organometallics, 1988.* ***17****: p. 815.*
13. *Silva, S.M.P.S., A. Z.; de Souza, R. F.; Dupont, J., J. Polym. Bull., 1998.* ***40****: p. 401.*
14. *Mehnert, C.P.C., R. A.; Dispenziere, N. C.; Afeworki, M., J. Am. Chem. Soc., 2002.* ***124****: p. 12932.*
15. *Zim, D.d.S., R. F.; Dupont, J.; Monteiro, A. L., Tetrahedron Lett., 1998.* ***39****: p. 7071.*
16. *Ansari, I.A.G., R., Org. Lett., 2002.* ***4****: p. 1507.*
17. *Kaufmann, D.E.N., M.; Henze, H. , Synlett., 1996: p. 1091.*
18. *Mathews, C.J.S., P. J.; Welton, T., Chem. Commun., 2000: p. 1249.*
19. *Mcnulty, J.C., A.; Wilson, J.; Dyck, J.; Adjabeng, G.; Robertson, A., Chem. Commun., 2002: p. 1986.*
20. *Rajagopal, R.J., D. V.; Srinivasan, K. V., Chem. Commun., 2002: p. 616.*
21. *Fukuyama, T.S., M.; Nishitani, S.; Sato, M.; Ryu, I., Org. Lett., 2002.* ***4****: p. 1691.*
22. *Park, S.B.A., H., Chem. Commun., 2004: p. 1306.*
23. *Handy, S.T.Z., X., Org. Lett., 2001.* ***3****: p. 233.*
24. *Yang, C.L.N., S. P., Organometallics, 2002.* ***21****: p. 1020.*
25. *Badri, M.B., J. J.; Perron, R., Tetrahedron Lett., 1992.* ***33****: p. 4435.*
26. *Yao, Q.Z., Y., Angew. Chem. Int. Ed., 2003.* ***42****: p. 3395.*
27. *Audic, N.C., H.; Mauduit, M.; Guillemin, J. C., J. Am. Chem. Soc., 2003.* ***125****: p. 9248.*
28. *Fischer, T.S., A.; Welton, T.; Woolf, J., Tetrahedron Lett., 1999.* ***40****: p. 793.*
29. *Stark, A.M., B. L.; Singer, R. D., J. Chem. Soc., Dalton Trans, 1999: p. 63.*
30. *Kim, D.C., D., Angew. Chem. Int. Ed., 2004.* ***43****: p. 483.*
31. *Carlin, R.T.O., R. A.; Wilkes, J. S.; Rovang, J., Inorg. Chem., 1990.* ***29****: p. 3003.*

32. *Carlin, R.T.W., J. S., J. Mol. Cat., 1990.* ***63****: p. 125.*
33. *Wikes, J.S.Z., M. J., J. Chem. Soc., Chem. Chem. Commun., 1992: p. 965.*
34. *Carlin, R.T.O., R. A., J. Electrochem. Soc., 1994.* ***141****: p. 1709.*
35. *Matyjaszewski, K.X., J., Chem. Rev., 2001.* ***101****: p. 2921.*
36. *Hawker, C.J.B., A. W.; Harth, E., Chem. Rev., 2001.* ***101****: p. 3661.*
37. *Kamigaito, M.A., T.; Sawamoto, M., Chem. Rev., 2001.* ***101****: p. 3689.*
38. *Guerrero-Sanchez, C.W., F.; Schubert, U. S., in Ionic Liquids in Polymer Systems. 2005, American Chemical Society. p. 37.*
39. *Carmichieal, A.J.H., D. M.; Bon, S. A. F.; Seddon, K. R., Chem. Commun., 2000: p. 1237.*
40. *Hong, K.Z., H.; Mays, J. W.; Visser, A. N.; Brazel, C. S.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D., Chem. Commun., 2002: p. 1368.*
41. *Harrison, S.M., S. R.; Haddleton, D. M., Chem. Commun., 2002: p. 2850.*
42. *Harrison, S.M., S. R.; Haddleton, D. M., Macromolecules, 2003.* ***36****: p. 5072.*
43. *Strehmel, V.L., A.; Wetzel, H.; Kraudelt, H.; Gornitz, E., Macromolecules, 2006.* ***39****: p. 923.*
44. *Zhang, H.H., K.; Mays, J. W.*
45. *Zhang, H.B., L.; Li, M.; Hong, K.; Visser, A. E.; Rogers, R. D.; Mays, J. W., in Ionic Liquids: Industrial Appication for Green Chemistry" 2001.*
46. *Zhang, H.H., K.; Mays, J. W. , in Ionic Liquids in Polymer System., R.B. Rogers, C. S., Editor. 2005.*
47. *Liu, Y.W., G.; Long, D.; Zhang, G., Polymer, 2005.* ***46****: p. 8403.*
48. *Liu, Y.W., G., Radiation Physics and Chemistry, 2005.* ***73****: p. 159.*
49. *Strehmel, V.K., H.; Wetzel, H.; Gornitz, E.; Laschewsky, A. .*
50. *Vygodskii, Y.S.M.n., O. A.; Lozinskaya, E. I.; Shaplov, A. S., Vysokomolekulyarnye Soedineniya, 2005.* ***47****: p. 704.*
51. *Haddlton, D.M.J., C. B.; Hannon M. J.; Shooter, A. J., Macromolecules, 1997.* ***30****: p. 2190.*
52. *Haddlton, D.M.C., C. B.; Dana, B. H.; Cuncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J., Macromolecules, 1999.* ***32****: p. 2110.*
53. *Biedron, T.K., P., J. Polym. Sci., Part A: Polym. Chem., 2005.* ***43****: p. 3454.*
54. *Ding, S.R., M.; Shen, Y., Macromolecules, 2005.* ***38****: p. 5921.*
55. *Sarbu, T.M., K., Macromol. Chem. Phys., 2001.* ***202****: p. 3379.*
56. *Ma, H.W., X.; Chen, X.; Zhou, Q., J. Polym. Sci., Part A: Polym. Chem., 2003.* ***41****: p. 143.*
57. *Ma, H.W., X.; Chen, X.; Zhou, Q., Polymer, 2003.* ***44****: p. 5311.*
58. *Zhang, H.H., K.; Mays, J. W., Polym. Bull., 2004.* ***52****: p. 9.*
59. *Ryan, J.A., F.; Zetterlund, P. B.; Yamada, B. , Macromol. Rapid Commun., 2004.* ***25****: p. 930.*
60. *Perrier, S.D., T. P.; Carmichael, A. J.; Haddleton, D. M., Chem. Commun., 2002: p. 2226.*
61. *Perrier, S.D., T. P.; Carmichael, A. J.; Haddleton, D. M., Euro. Polym. J., 2003.* ***39****: p. 417.*
62. *Vijayarahgavan, R.M., D. R., Aust. J. Chem., 2004.* ***57****: p. 129.*

63. *Zhao, Y.Z., J.; Chen, C.; Xi, F., J. Polym. Sci., Part A: Polym. Chem., 2002.* ***40****: p. 3360.*
64. *Zhang, H.H., K.; Mays, J. W., Macromolecules, 2002.* ***35****: p. 5738.*
65. *Zhang, H.H., K.; Jablonsky, M.; Mays, J. W., Chem. Commun., 2003: p. 1356.*
66. *Harwood, H., J. Macromol. Sci. Macromol Symp., 1987.* ***10/11****: p. 331.*
67. *Csihony, S.F., C.; Bruneau, C.; Horvath, I. T.; Dixneuf, P. H., New J. Chem., 2002.* ***26****: p. 1667.*
68. *Xiong, Y.F., L.; Shen, Z., Cuihua Xuebao, 2006.* ***27****: p. 75.*
69. *Kadokawa, J.I., Y.; Tagaya, H., Macromol. Rapid Commun., 2002.* ***23****: p. 757.*
70. *Naudin, E.H., H. A.; Branchaud, S.; Breau, L.; Belanger, D., J. Phys. Chem. B, 2002.* ***106****: p. 10585.*
71. *Sekiguchi, K.A., M.; Fuchigami, T., J. Electroanal. Chem., 2003.* ***557****: p. 1.*
72. *Pringle, J.M.E., J.; Howlett, P. C.; MacFarlane, D. R.; Chaplin, A. B.; Hall, S. B.; Officer, D. L.; Wallace, G. G.; Forsyth, M. , Polym., 2004.* ***45****: p. 1447.*
73. *Wagner, K.P., J. M.; Hall, S. B.; Forsyth, M.; MacFarlane, D. R.; Officer, D. L., Synthetic Metals, 2005.* ***153****: p. 257.*
74. *Klingshirm, M.A.B., G. A.; Holbrey, J. D.; Shaughnessy, K. H.; Rogers, R. D., Chem. Commun., 2002: p. 1394.*
75. *Robinson, K.L.K., M. A.; Paz Panez, M. V.; Wang X. S.; Armes, S. P. , Macromolecules,* ***2001****.* ***34****: p. 3155.*
76. *Mastrorilli, P.N., C. F.; Gallo, V.; Suranna, G. P.; Farinola, G., J. Mol. Cat. A: Chem., 2002.* ***184****: p. 73.*
77. *Masahiro, Y.O., H. , Chem Lett., 1999.* ***9****: p. 889.*
78. *Masahiro, Y.O., H. , Electrochemi. Acta., 2001.* ***46****: p. 1723.*
79. *Masahiro, Y.O., W.; Ohno, H. , Polym. Adv. Technol., 2002.* ***13****: p. 589.*
80. *Ogihara, W.W., S.; Nakajima, H.; Ohno, H., Electrochemi. Acta., 2006.* ***51****: p. 2614.*
81. *Tang, J.S., W.; Tang, H.; Radosz, M.; Shen, Y., Macromolecules, 2005.* ***38****: p. 2037.*
82. *Tang, H.T., J.; Ding, S.; Radosz, M.; Shen, Y., J. of Polym. Sci., Part A: Polym, Chem,, 2005.* ***43****: p. 1432.*
83. *Billaud, C.S., M.; Bolte, M., Eur. Polym. J., 2000.* ***36****: p. 1401-1408.*
84. *Montheard, J.C., M.; Chappard, D.; , JMS-Rev Macromol Chem Phys, 1992.* ***C32****: p. 1.*
85. *Sogah, D.Y.H., W. R.; Webster, O. W.; Cohen, G. M., Macromolecules, 1987.* ***20****: p. 1473.*
86. *Beers, K.L.B., S.; Gaynor, S. G.; Matyjaszewski, K., Macromolecules, 1999.* ***32****: p. 5772.*
87. *Fuji, Y.W., K.; Baek, K. Y.; Ando, T.; Kamigaito, M.; Sawamoto, M., J. Polym. Sci., Part A: Polym. Chem., 2002.* ***40****: p. 2055.*
88. *Sato, T.M., J.; Otsu, T., J. Polym. Sci., Part A: Polym. Chem., 1984.* ***22****: p. 3921.*
89. *J. Pacansky, R.J.W., Proc. Water-Borne Higher Solids Coat. Symp., 1989.* ***175****: p. CA: 111: 195538.*
90. *J. Lebduska, J.S., K. Kaspar, Chem. Prum., 1986.* ***36****: p. 472.*

VITA

Xiao Ma was born in Changsha, Hunan province, CN on February 8, 1981. She went to high school at the First High School of Changsha in the same city. In 2003, she graduated from East China University of Science and Technology in Shanghai with a Bachelor of Engineering degree after the four years of undergraduate study.

In Aug 2003, she was admitted as a graduate student in the Department of Chemistry, University of Tennessee, Knoxville. She earned her Master of Science degree in Chemistry with a Polymer Chemistry concentration in August 2006.